Experimental Testing of New Generation Chemicals and Conventional Surfactants as Additives to Steam Injection

by

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Abstract

With the decrease in nonrenewable energy sources, heavy oil and bitumen recovery gains more attention due to their huge potential. The recovery of heavy oil or bitumen requires viscosity reduction where steam is commonly injected to mobilize and displace viscous oil. This application, however, has several disadvantages including high water demand, big energy consumption for steam generation, and carbon footprint. To minimize these drawbacks and improve process efficiency, chemicals can be added to the steam.

Chemical additives, specifically surfactants and caustic, to steam applications was initially considered in the 80's (Castanier and Brigham, 1991), but later lost attention due to high cost and difficulties in finding thermally stable agents. As steam applications become more fashionable and new techniques such as Steam Assisted Gravity Drainage (SAGD) has been developed, research on chemical additives has regained attention. This study dealt with an experimental investigation of different chemicals to high temperature processes and outlines advantages and disadvantages of the candidates (cost, increase in oil recovery, etc.). The chemical database created in this project can be categorized into solvents (hydrocarbon and water-soluble solvents), surfactants (anionic and non-ionic surfactants), caustic injection (high pH solution), ionic liquids, and nanofluids.

Thermal stability of the additives is one of the major challenges. Commercially available chemicals were tested on thermal stability using Thermogravimetric Analysis (TGA) where the decomposition of the chemical is measured by mass over constant temperature increase (up to 400°C). Non-ionic surfactants exhibited good thermal stability compared to anionic surfactants. Selected chemicals were then assessed on steam-to-oil (SOR) ratio by developing steam injection experiments on sandpacks. The changes in the SOR were quantified by measuring the increase in oil recovery. The observed performance improvements were compared with the commercial prices and the equalized injected concentration of the chemicals to conclude the screening of the chemical dataset. It was shown that heptane and biodiesel were the most efficient chemicals in terms of SOR and price. Assumptions were made related to the flow parameters effected by the chemicals.

To further investigate the mechanics of the recovery improvements process with chemicals, a visual Hele-Shaw model was developed. These experiments confirmed some key theories drawn by the sandpack experiments such as the emulsification and interfacial tension (IFT) reduction by surfactants, asphaltene precipitation and the viscosity decrease by hydrocarbon solvents, wettability alteration by ionic liquids etc. Lastly, further screening procedures were emphasized for future research to optimize the implementation factors (such as concentration or injection strategies) as well as for quantification of improved flow parameters (such as IFT reduction or emulsification).

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Chapter 1

Introduction

A production cycle of an oil and gas reservoir is categorized into the three phases primary, secondary and tertiary recovery. The primary recovery refers to the first period of the production where naturally stored energy, such as pressure, forces the oil to flow into the wellbore. With the depletion of this energy, artificial energy is applied from the surface into the field to continue the oil production. These secondary recovery mechanisms can be accomplished by injection gas for pressure maintenance or water for displacing the oil into the formation. Once the economical limit is reached, novel technologies can be combined with secondary recovery methods to lift the stagnating oil recovery. These tertiary or enhanced oil recovery (EOR) methods are specifically designed for the depleted fields and may not be economically feasible. The complexity and characteristics of heavy viscous oils and oil sands result in low efficiency of primary and secondary recovery methods.

Canada is a good example of extensive heavy-oil sources and two main methods are intensively used as recovery methods in this country: open-pit mining and in-situ recovery. Open-pit mining is applicable only in shallow formations (depth of less than 60m) and extraction process yields recoveries up to 90% (Banerjee, 2012). When the reservoir depth is too high (>75m), in-situ operations are exercised. High mobility ratio due to the viscous nature of oil as well as the low gas solubility set the trend of applying unconventional recovery methods in heavy oil fields. In-situ applications can be categorized as thermal (steam, in-situ combustion, and electrical heating) or non-thermal (gas, chemical and microbial) EOR. Table 1.1 shows some examples of the in-situ methods utilized in heavy oil fields. This thesis focuses on steam injection which is reviewed in the following section. For general evaluation of non-thermal methods, one may be referred to Speight (2009), Farouq Ali (2006), Lake (1989) and Donaldson et al. (1985).

Thermal EOR Methods

Instabilities in the displacement by a low viscous fluid requires an injection of high volumes into the reservoir. This is caused by unfavorable mobility ratio, which is defined as the ratio of the mobility

Table 1.1: Examples of thermal and non-thermal recovery methods utilized in heavy oil fields

Thermal Methods	**Non-Thermal Methods**
Steam Flooding	Polymer Flooding
Cyclic Steam Stimulation (CSS)	Surfactant Flooding
Steam Assisted Gravity Drainage (SAGD)	Alkine/Caustic Flooding
In-Situ Combustion	Immiscible CO_2 Flooding
Hot Waterflooding	Waterflooding
	Cold Heavy Oil Production (CHOPS)

of the displacing fluid to that of the displaced fluid. If water with a viscosity of 1 cP is injected into a heavy oil reservoir where the oil phase has a viscosity of at least a 1000 cP, unfavorable conditions trigger viscous fingering and an inefficient displacement of heavy oil. Several methods can be utilized to minimize this difference by either increasing the viscosity of the displacing fluid or decreasing of the displaced fluid's viscosity. Bringing energy into the reservoir as heat leads to a high oil viscosity reduction from 1000 cp (at 25°C) to around 1 cp at a temperature of 177°C (Farouq Ali, 2006). As a result, the mobility ratio would decrease, and the oil can be displaced efficiently without instabilities at the interface.

The desired effect of thermal recovery techniques is as simple as explained above. However, the process and mechanics of injecting steam or hot water into the reservoir is a challenging process due to technical complexities and economic limitations. The transferred heat into the rock and fluids leads to high temperature variations and phase changes at specific positions. Besides the heat transfer, gravity segregation is another important effect of oil displacement by steam. When injecting steam into the formation, the lighter gaseous phase tends to flow towards the upper part of the formation due to the density difference. After the oil is mobilized and the steam is spread over the top of the formation, the steam zone expands in a downwards direction. The injection of steam exhibits a low vertical sweep which is the result of the non-stable steam front. However, the segregation and the non-frontal displacement of oil is advantageous because the injection pressure can be minimized. This leads to higher efficiency in heat transfer which is initially conductive and later convective (Farouq Ali, 2006). The described process is a typical example for a multi-well (injection\producer) design in a heavy oil reservoir. There are different techniques of producing heavy oil by steam displacement. There are other techniques of producing heavy oil by steam displacement. A well-known example is Steam Assisted Gravity Drainage (SAGD), first introduced by Butler (1991).

SAGD is a well known and popular steam injection method for viscous heavy oil in-situ recovery. The upper injection well transfers the steam into the reservoir while the lower production well produces heavy oil and condensate predominantly by gravity. The space between those two wells is typically around five meters. Constant injection of the steam creates a chamber around the injection well. Because of gravity segregation, this chamber expands in an upward and lateral direction. The high temperature steam transfers the heat into the oil phase and its surroundings at the boundaries of the chamber by thermal conduction. The mobilized oil and steam condensate drain then downwards along the steam chamber in a counter-current manner. The liquid mixture of condensate and oil are then produced through the lower well where separation and water treatment processes are followed above surface. It is very crucial to circulate in a start-up phase steam through the two wells to initiate the growth of the steam chamber with high efficiency. The formation and the hydrocarbons are heated surrounding the wells until a fluid communication is established.

The main drawback of the SAGD method is the overall efficiency. Any attempt to reduce the amount of steam would improve not only the economic feasibility but also the environmental effects.

1.1 Statement of Problem and Methodology

EOR projects bear challenges and drawbacks related to feasibility of the field implementation. Especially steam injection techniques require special attention to improve feasibility due to high cost of injectant. Steam-oil-ratio (SOR), described as the volume of steam needed to produce a volume of oil, should be reduced by improving recovery or reducing the amount of steam injected. Techniques of combining chemicals with steam injection have gained wide recognition in the petroleum industry as a solution in improving the efficiency, reducing the SOR. The main problem is to find suitable chemicals as steam additives. In general, it can be said that a suitable chemical for thermal EOR techniques needs to retain its properties under high temperature and pressure. Moreover, the cost of the chemical should not be a limiting factor to maintain economic feasibility. Finding suitable candidates as chemical additives to the SAGD process requires a standardized screening procedure. Critical parameters to be considered in this screening process should be well understood and scrutinized for successful screening process. The challenges related to thermal recovery techniques and utilization of a chemical additive are described in the following.

Challenge 1: Thermal Stability

Thermal stability of a chemical is described by the temperature that is needed to initiate decomposition of the chemical compounds. As heat is supplied to trigger these reactions, changes in the properties can be quantified, such as increase in vapor pressure when the molecules break into fragments, weight loss, viscosity change and heat of reaction (Blake et al., 1961). Thermogravimetric analysis (TGA) is commonly used to measure the limits of exposure in critical temperature environments for materials. During this analysis, the mass of the material is measured over time with a controlled heating rate and a controlled atmosphere. A standardized test report is summarized in ASTM E2250-17. Mass of the tested product drops after the distinct onset temperature (T_0) is reached. This indicates that heat is released by an occurring endothermal reaction of the material and the mass continues to change with increasing temperature. There are different methods of measuring the thermal stability of chemicals, such as freezing point depression where the change in molar weight of a compound can be calculated.

Challenge 2: Screening of Chemical Mechanics and Parameter Sensitivity under High Temperatures

Uncertainties of the physics and the mechanics while injecting a chemical additive under high temperatures slows down the development in this research area. One of the reasons is the limitations of laboratory equipment or expenses for expensive resources required to investigate and simulate accurately heavy oil recovery by steam injection. Therefore, proper screening procedures of chemicals are not well established for elevated temperatures. Sensitivity of a suitable chemical may vary with the specific reservoir and production parameters, such as clay content, oil composition, water salinity, reservoir temperature, etc. Especially the impact of a chemical in a SAGD operation is ambiguous due to the lack of knowledge in the potentially improving parameters (steam chamber growth, oil drainage, emulsification etc.).

Challenge 3: Type of Chemical

When designing a field application of thermal EOR process in combination with a chemical, the additive is required to retain its properties under high temperatures. The cost of the chemical is another limiting factor. Moreover, each chemical type require different way of handling and proper injection strategy should be adapted based on the physics of the displacement process. In the following sub-sections, candidates for the combination of chemicals with thermal processes are summarized with their primary mechanisms coupled with SAGD operations.

Solvents

As described in the previous section, high mobility differences between viscous oil and the displacing fluid result in unfavorable displacement conditions. Together with thermal diffusion of the steam, an injection of a solvent can further reduce the viscosity of the heavy oil by dissolving into the oil phase. The most common solvents are light alkanes, such as propane, butane, pentane, etc. Nasr et al. (2002a) tested different condensable hydrocarbon solvents (C_3 to C_8) by co-injecting it with steam. The oil rate increased with the increase in carbon number where hexane (C_6H_{16}) showed the highest recovery. Nasr et al. (2002a) stated that a suitable solvent should be designed based on the vaporization temperature being close to the steam temperature. However, the screening process requires a consideration of more parameters besides injection temperature, such as reservoir characteristics (oil sand composition), oil composition, and cost and availability of the solvent (Marciales and Babadagli, 2016).

When injecting a solvent, the following advantages can be expected according to Gupta et al. (2005) based on Solvent Aided Processes (SAP):

- Improved economics due to accelerated production rates and corresponding cash flow
- Reduced environmental impact because of reduction in heat and fuel requirements for steam generation
- Asphaltene precipitation and upgrading of produced oil
- Higher recovery factor with less steam requirement leading to improved SOR

When asphaltene is removed by injection of a non-polar hydrocarbon (pentane or heptane), the viscosity decreases with a high efficiency (Ilyin et al., 2016). One goal of solvent injection is to retrieve as much of the injected volume as possible and re-use it for future applications to improve the economics due to the high costs of hydrocarbon solvents. More volatile, gaseous hydrocarbons, such as butane and propane, are less expensive but can lower the temperature of the chamber edge during co-injection preventing improvements in oil mobility (Keshavarz et al., 2015). Because of these drawbacks, Sheng et al. (2017a) suggested to use a water soluble solvent due to high potential in retrieval with the high water production compared to oil combined with improvements in bitumen mobility by heat and dilution. Dimethyl ether (DME) was investigated as a water soluble solvent in comparison with butane (C_4H_{10}) in a simulation study. It was shown that the chamber-edge temperature is higher with DME than with butane. Furthermore, the solvent recovery was approximately 15% higher but the ultimate recovery and SOR were lower in contrast to the butane co-injection. Water-soluble solvents can be promising in terms of solvent retrieval and mechanics of heat transfer along the chamber; however, more experiment investigations are required specifically at the lab scale to prove the economical advantages over alkane-based solvents.

Surfactants

Surfactants can be divided into four groups (as listed in Table 1.2) (Butt et al., 2006) based on the charge of the the hydrophilic groups of the molecules. The hydrophilic part of an anionic surfactants is negatively charged and can be for instance a carboxylate, sulfonate or sulfate group. For a cationic surfactant, the molecules have a positive charged hydrophilic group while the non-ionic surfactants are not charged. A more expensive surfactant carries a positive and negative charge and is referred to amphoteric surfactants.

Table 1.2: Types of surfactants with common examples

Type of Surfactant	**Charge Hydrophilic Group**	**Common Surfactants** (Butt et al., 2006)
Anionic	Negative	Sodium alkylsulfate, Sodium alkylether sulfate, Sodium alkylcarboxylate
Cationic	Positive	Alkyltrimethylammonium bromide\chloride, Dialkyldimethylammonium bromide
Nonionic	No charge	Alkylethylene glycol, Poly(ethylene oxide)
Amphoteric\ Zwitterionic	Positive + Negative	Alkyldimethylpropanesultaine

Considering a two-phase system with immiscible fluids in equilibrium, the surfactant adsorbs at the phase boundary lowering the free energy. The amount of work required to expand the interface of the two phases is the interfacial free energy per unit area which is referred to interfacial tension (IFT) γ $[mJm^{-2}$ or $mNm^{-1}]$ (Tadros, 2013a). The IFT is lowered when the surfactant attaches with the hydrophobic and hydrophilic at the interface. When the displacing fluid (e.g. water) is injected into an oil saturated reservoir, many driving forces (gravity, viscosity, capillarity) and parameters (heterogeneity, compaction etc.) control the efficiency of oil recovery and residual oil saturation. Injecting a surfactant would ultimately increase displacement efficiency by attaching to the phase boundaries to lower the IFT.

When applying a surfactant with high temperature processes, several criteria should be met. Gupta and Zeidani (2013a) stated the following required properties of a surfactant under steam conditions:

- Effective reducing IFT
- Alteration of reservoir wettability to water-wet conditions
- Capable of being vaporized
- Thermally stable
- Able to stabilize oil-in-water (O/W) emulsions
- Compatible with formation water

When supplying heat to cold oil phase by thermal conductivity along the interface of oil/steam/condensate, IFT reduction occurs without adding a surfactant into the process. Heat increases the entropy of the system due to gain in random activity by the molecules. This causes a decrease in the Gibbs free energy and, therefore, a decrease in IFT between the two liquids. An effective surfactant can further decrease the IFT between the phases and stabilize the O/W emulsions. Emulsification have a great impact in flow behavior of thermal stimulation processes and can affect efficiency of hydrocarbon recovery. The most two common types of emulsions in the oilfield are oil-in-water (O/W) and water-in-oil (W/O). The formation of O/W emulsions includes a benefit in production efficiency due to lower viscosities and higher drainage rates compared to the W/O emulsions (Taylor, 2018).

Surfactants can also be used as foaming agents for conformance control in SAGD. Chen et al. (2010) simulated co-injection of a surfactant solution with steam for uniform steam chamber growth to solve issues related to bypassing of oil-bearing regions caused by gravity segregation and viscous fingering. Foam stability is one of the major uncertainties in this application. Cuenca et al. (2014) designed and tested surfactants with foam boosters on foam stability under high temperature and high pressure based on screening method presented by Chabert et al. (2013) to visualize foaminess in a cell. The formulated steam foamers (surfactant + foam booster) showed improved half-life indicating higher stability compared to pure surfactants. However, this formulation needs to be further tested in dynamic experiments.

The screening and selection criteria for suitable surfactant is very important to impact the efficiency of steam injection processes. The elevated temperature environment sorts outcauses deterioration a high quantity of surfactants. These chemicals are also sensitive toFurther on, formation water with the properties of salinity of the formation water and pH of the environment are important influencing parameters in surfactant design. Specifically, ionic surfactants characteristics change with pH of the brine solution. With a higher salinity, electrostatic repulsions between the surfactant head groups is reduced leading to a lower critical micelle concentration (CMC) and higher surfactant stability (Butt et al., 2006). In fact, high pH alkaline flooding is a well-known approach to utilize the natural surfactants in the heavy oil. This process was studied for heavy oil applications by the references Haas et al. (2013), Liu et al. (2006), and Tang et al. (2013). Knowing the brine composition together with the chemical characteristics of the surfactant is crucial in designing a productive field application.

Nanoparticles

A novel approach of EOR methods is the injection of solid particles (nanoparticles) with sizes ranging from 1 to 100 nm. To date, this research area carries a number of uncertainties. Therefore, it is still at the laboratory scale development and has not been tested in the field commercially. Sun et al. (2017a) reviewed the progress in this area and categorized nano material applications under three different techniques: nanofluids, nanocatalysts and nanoemulsions. When injecting a nanofluid, the solid particles are in colloidal suspension in a base fluid. Nanoparticles stabilize emulsion to create nanoemulsions that are capable of withstanding demanding conditions and remain stable (Binks and Lumsdon, 2000; Sun et al., 2017a). Aquathermolysis, which are chemical reactions that upgrade heavy oil to lighter products, are triggered by metal nanoparticles, such as nickel or iron. These nanocatalysts catalyzes breaking of carbon-sulfur bonds with asphaltenes (Hashemi et al., 2014; Hyne, 1986; Sun et al., 2017a) which reduce viscosity (Shokrlu and Babadagli, 2011). The EOR mechanisms related to the introduction of nanoparticles into the reservoir can be listed as following (Sun et al., 2017a):

- Generation of a disjoining pressure
- Pore channels plugging
- IFT reduction
- Wettability alteration
- Emulsification (nanoemulsions)
- Catalyzing Aquathermolysis with viscosity reduction (nanocatalysts)

As highly surface active particles, these mechanisms can impact oil recovery. So far, researchers tested a pool of nanoparticles consisting of Al_2O_3, SiO_2, Fe_2O_3, where SiO_2 in combination with other particles achieved better results (Cheraghian and Hendraningrat, 2016a). Nanotechnology can be considered as a promising strategy to increase project economics by the listed improvements. However, injectivity of the particles is a challenging task as the particles aggregate due to strong Van der Waals interaction (Sun et al., 2017a) and can cause plugging of pipes or other surface facilities. Cheraghian and Hendraningrat (2016a,b), Hashemi et al. (2014), Sabet et al. (2016), and Sun et al. (2017a) provided detailed review on the application of nanoparticles in the oil industry with updates in current research milestones.

1.2 Aims and Objectives

This research project aims to screen chemicals in their efficiency in improving heavy oil displacement by different experimental methodologies. These additives include a majority of the previously discussed chemicals which can be categorized as solvents (DME, heptane), non-ionic and anionic surfactants, nanoparticles and high pH solutions. The following are the main objectives of this research:

- Designing laboratory setups and establish methodologies to accurately predict and interpret injection of chemical additive under high temperature.

- Selecting and testing different chemicals based on previous projects and researching about potential impacts on heavy oil recovery.
- Quantifying the efficiency of the chemical additive injection into porous media based on incremental oil recovery. Coreflood experiments with artificial sandpack experiments are planned to measure these potential improvements caused by distinct chemical mechanics.
- Studying the effects of injecting a chemical in heavy oil recovery by thermal displacement using visual Hele-Shaw models. Visualization of steam/chemical/oil flow using different injection patterns should lead to the interpretation of improved parameters to steam injection, such as IFT, emulsification, viscosity reduction etc.
- Suggesting chemical screening procedures for steam applications based on chemical sensitivity to the exposed injection and reservoir conditions.

1.3 Structure of the Thesis

This paper-based thesis includes four chapter. Chapter 2 and Chapter 3 consist of two conference papers presented through this research project and submitted for peer review.

Chapter 1. This chapter introduces the reader into this thesis. Principles of thermal recovery techniques are discussed first followed by the challenges of chemical additives to steam injection. Furthermore, the objectives of this research project are outlined .

Chapter 2. Thermal stability tests of the chemicals as well as coreflood experiments were conducted to quantify the performance of steam injection with chemicals. The additive was injected at room temperature into the hot tubing to vaporize and mix with the steam at a temperature of 200°C. Chemical additives included anionic and non-ionic surfactants, ionic liquid, high pH solution, solvents, a biodiesel and a nanofluid. Assumptions were made for the potential impact of enhancing heavy oil drainage.

Chapter 3. Interpretation of the effects related to the chemicals injected in the coreflood experiments are discussed in this chapter. Visualization of steam/condensate/oil interface propagation in a Hele-Shaw model led to an accurate understanding of what primary mechanisms are affected by chemical additives to steam injection.

Chapter 4. Chapter 4 concludes this study together with suggestions for future work related to the research area of chemical additives to steam injection.

Chapter 2

Recovery Improvement of Gravity Driven Steam Applications Using New Generation Chemical Additives

This paper is a revised and modified version of the paper SPE-18714 presented at the SPE Western Regional Meeting held in Bakersfield, California, USA, 23-27 April 2017.

2.1 Preface

Reservoirs containing very heavy oil or extremely heterogeneous/fractured geology are not convenient for steam flooding and even cyclic steam injection. Then, steam can be used to heat the reservoir and accelerate the recovery by gravity drainage. Two well-known applications of this method are steam assisted gravity drainage (SAGD) and thermally assisted gas oil gravity drainage. Although the latter is not commercially applied, the former is a proven technology with remarkable production in Canada and Venezuela. Due to the risks caused by cost and solvent retention, no large-scale applications of solvent injection with steam have been implemented. An alternative is to use chemicals as suggested a few decades ago to alter the interfacial forces and improve microscopic displacement. This paper presents experimental results on testing -the new generation- chemicals for their capability in recovery improvement.

Sandpack experiments were conducted to evaluate the incremental in oil recovery by chemical additives compared to sole steam injection. Steam and chemicals were heated and introduced to the system from separate channels at the entrance of the vertically situated sandpack (30 cm long, 5 cm in diameter). The chemicals used include thermally stable surface agents, such as anionic surfactants (AAS J1111, O352, LTS-18), non-ionic surfactants (Tween80/85, Span80/85, Novelfroth190, Triton X-100), a biodiesel (FAME), ionic liquid (BMMIM BF4), high pH solution (NaBO2), solvent (heptane, DME), and nanoparticles (SiO2). The oil selected was 27,000 cp crude.

Incremental recoveries were monitored and related to the thermal stability and commercial prices of the chemicals. A comparative analysis was provided as to their contribution to the reduction of the cost (lower SOR) and chemicals were classified based on their recovery improvement performance and thermal stability using thermogravimetric analysis (TGA). Through this experimental schematic, the highest increase in oil recovery was achieved by heptane which was also cheap in comparison to the other tested chemicals. Asphaltene precipitation was quantified by conducting SARA analysis of samples taken from the coreflood experiments. The nanoparticle was placed initially into the core holder and had the second-best performances in the steam-to-oil ratio (SOR). Biodiesel did also improve oil recovery, but the effects need to be further investigated. The non-ionic surfactants showed great thermal stability and Span80, Tween80, as well as Novelfroth190, lowered the SOR by improving oil recovery. On the other hand, the injection of LTS-18 as anionic surfactant showed an increment of ultimate oil recovery by around 3%. As a wettability modifier, the ionic liquid proved to be profitable in rising oil recovery from the sand pack experiment in a tertiary and an initial injection attempt. However, the ionic liquid is the most cost-effective chemical from the tested candidates.

Keywords: Steam injection, gravity dominated flow, chemical additives, emulsification, interfacial tension and drag reduction

2.2 Introduction

Heavy oil and bitumen deposits have a major contribution to the world's crude oil resources and are receiving more attention due to the gradual decrease in conventional oil reserves. Thermal recovery techniques were developed for deep reservoirs where open-pit mining is not feasible. Steam injection processes, such as steam-assisted gravity drainage (SAGD), cyclic steam stimulation (CSS) or steam flooding, are commercially applied to produce heavy oil. It is proven through numerous studies and field applications that the gravitational drainage results in highly efficient oil recovery (Al-Bahlani and Babadagli, 2009; Butler and Mokrys, 1989; Butler and Mokrys, 1991; Gupta and Zeidani, 2013b; Zhao et al., 2005). The economic and environmental aspects related to the thermal recovery techniques have the greatest impact in implementing a profitable field implementation. Reducing cumulative steam-oil ratio and/or improving the recovery rate by additives result in the improvement of the efficiency of steam applications.

Additives to steam have been studied over a few decades for different purposes. Castanier and Brigham (1991) summarized the field tests of cyclic steam stimulation and steam injection processes conducted with chemical additives during the late 1970s and 1980s. The authors outlined the success of some field implementations connected to high efficiencies and economically favourable conditions of additives with steam. Keijzer et al. (1986) investigated surfactants in an extensive laboratory study as preparation for a steam-foam field pilot test. For the high temperature (210°C) and high pressure (305 psi) steam injection, alkyl toluene sulfonate was used and achieved steam diversion towards the unswept areas. Furthermore, a field application of cyclic steam stimulation with caustic injection (sodium metasilicate) was reported by Mbaba and Caballero (1983). The in-situ generation of surfactants by acidic crudes yielded a significant recovery improvement in the late cycles of the steam soak project.

Various chemicals with specific mechanisms have been proposed and studied to achieve incremental in oil recovery. In this exercise, the main task was to investigate improvements in driving forces contributing to oil flow in thermal applications caused by adding chemicals to steam. Capillarity and gravity represent the physical forces mobilizing the oil towards the producer (Mohammadzadeh et al., 2012). Gravity is especially supposed to be the dominant force in the gravity drainage flow regimes, which is typically the result of the density difference of the two phases (i.e., gaseous and oleic). In contrast, the buoyancy force of the vertical rising steam chamber can cause a fingering phenomenon (Al-Bahlani and Babadagli, 2009). Solvent-Aided SAGD processes (SA-SAGD), such as Expanding Solvent-SAGD (ES-SAGD) introduced and patented by Nasr et al. (2002b) and Nasr and Isaacs (2001), Steam Alternating Solvent (SAS), and Solvent Aided Processes (SAS) are advanced operations of gravity drainage driven flows. The concept of SA-SAGD is to co-inject solvents (hydrocarbons, i.e., hexane) with steam. The solvent flows with the steam along the boundary of the steam chamber to dissolve into the oil phase for reduction of oil viscosity (Nasr et al., 2002b; Nasr and Isaacs, 2001).

(Naderi et al., 2015) investigated the effects of bitumen viscosity and bitumen-water IFT on steam assisted bitumen recovery by conducting pressure cooker tests. Solvent addition (hydrocarbon, pentane) reduced the ultimate bitumen recovery whereas the IFT reduction with the addition of biodiesel (e.g. fatty acid methyl esters) led to an insignificant increment in oil recovery. By considering the capillary number and bond number, the gravity force and viscous forces should be promoted with the reduction of IFT. However, the capillary number increases with decreasing viscosity. The costs for the chemical composition as well as the retrieval are important aspects for the feasibility of field applications.

Many SAGD operations are becoming aged and need low cost and effective solution to maintain the production. Meanwhile, steam applications in fractured reservoirs (especially carbonates) require further attempts to improve matrix-fracture interaction. Therefore, the use of new generation chemicals (in addition to proven surfactants) is essential in maintaining efficiency and reducing the steam cost/amount. This paper addresses these issues with suggestions to industry and also suggests new ideas for further research. We specifically investigated new chemical agents and its effects on heavy-oil recovery by gravity drainage through coreflood experiments. The chemicals were selected based on previous studies with the appropriate available data (Cao et al., 2015, 2017; Mohammed and Babadagli, 2014, 2015; Wei and Babadagli, 2016, 2017). The results and the specific properties of these chemicals are discussed with some suggestions for further research and potential field applications.

2.3 Experimental Materials

Dynamic sandpack experiments were conducted to simulate oil drainage driven by gravitational flow under high-temperature steam flow conditions. For this study, a heavy crude oil sample with a viscosity of 27,000 cp and a density of 0.99 $[g/cm^3]$ at temperature 25°C was used. The detailed schematic of the experimental apparatus is given in Figure 2.1.

Steam was generated inside an oven with a temperature of 200°C and introduced together with

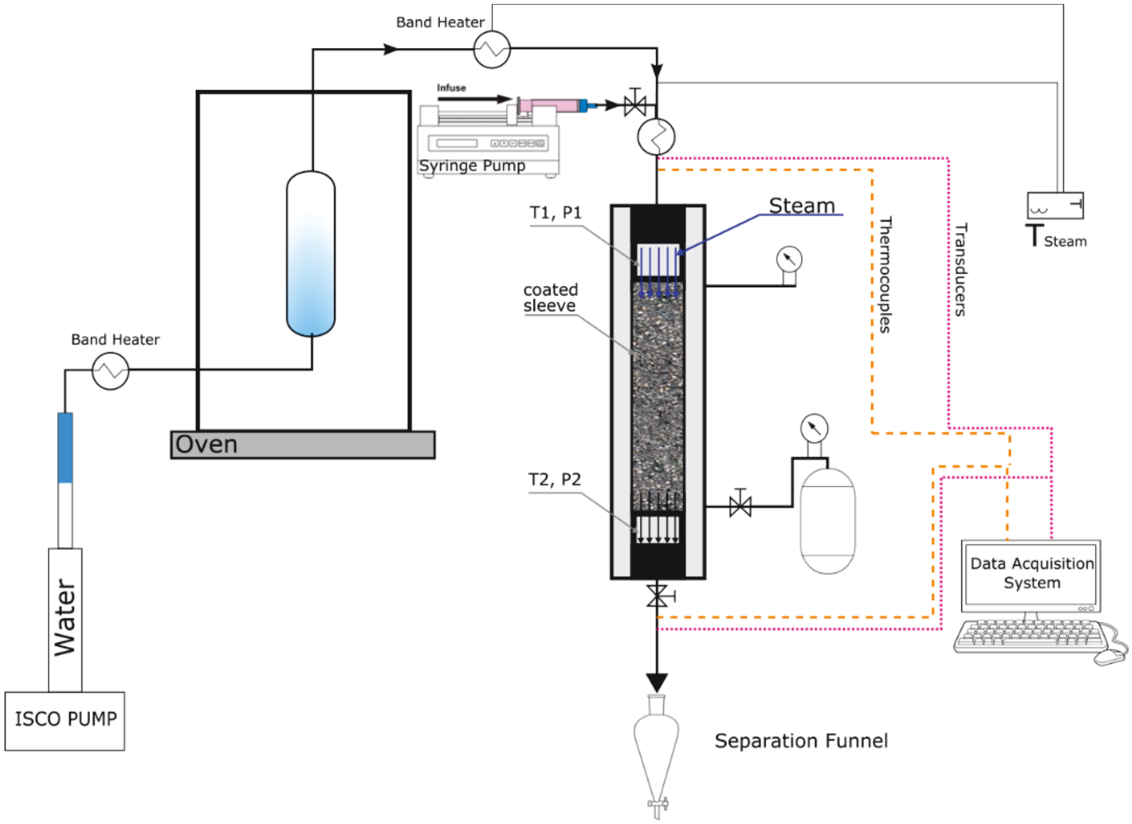


Figure 2.1: Schematic of the dynamic sandpack experiments.

the cold chemical from a separate channel using a syringe pump with a low flow rate. The second channel allows a tolerance in examination of different chemical quantities as well as different injection strategies. The steam and the heated tubing vaporize the chemical solution to a similar temperature of the steam phase. With the temperature environment of 200°C and atmospheric pressure, saturated low pressure steam was injected into the core. The vertically positioned core holder ensure a gravity dominated system (pressure difference 1-15 psi). Overburden (250-300 psi) was applied on the sleeve inside the core holder and the sleeve was coated with 500μm sand grains to minimize steam slippage along the sides of the sleeve. Transducers and thermocouples recorded the temperature and pressure of the gaseous phase at the entrance and the exit of the core. The recovered oil was measured using separation funnels. The produced samples were mixed with toluene to increase density difference and separated by gravity. After water removal, the oil recovery was measured by weight.

As a preliminary study, injection of a high-pressure steam was tested using a similar methodology with a lower concentration of 1-1.5%wt. The schematic of this experiment can be seen in the Appendix Figure A.2. A manually controlled backpressure regulator at the outlet kept the pressure difference small to achieve a gravity dominated flow. The chemical was co-injected with steam as well as injected as a tertiary process using a second ISCO pump. The results showed high deviations in pressure which led to the decision of modifying the methodology to a low-pressure injection to obtain the highest accuracy with least errors (Appendix Figure A.3). Therefore, this method was considered as an initial attempt for a chemical screening process for additives to improve gravity driven steam applications. Any match in results is still accounted and explained in the next section.

Preparation of sandpack. The artificial sandpack was fully saturated with oil and has an approximate porosity of 0.32 with the utilized packing procedure. The sand was sieved with a sieve shaker to a grain size range of $300 - 500 \mu m$. Then, it was mixed with the heavy oil at a fixed ratio for all experiments and left at anaerobic conditions for 24 hours. The coreholder encloses a core with the dimension of 4 inch length and 2 inch diameter. The oil sand was loaded in the sleeve in layers and compressed manually. The strength applied and the intervals of compressing the oil sand was tried to be the same in all models to ensure that the samples are identical.

Uncertainties of experiment and assumptions. As can be realized, the experimental procedure is highly difficult to duplicate due to the nature of the process (it is highly sensitive to temperature and pressure drop). Especially, using totally different nature of chemicals makes this process even harder for comparative analysis. Utmost attention was paid to maintain the same steam conditions (rate, pressure drop, temperature) in all cases. The reference tests were repeated numerous times and analyzed statistically to guarantee confidence in the evaluation. Hence, any deviation from the reference case can be attributed to the positive or negative effect of the additive.

Permeability and porosity values deviate significantly in an artificial sandpack when an inconsistent packing method is chosen. In this procedure, it was done in layers and the compression strength was applied simultaneously to each layer to ensure homogeneous distribution. A more accurate result could have been achieved by following the standard test method for compaction characteristics ASTM D698-12 where a hammer is dropped from a specified height to apply consistent strength on the oil sand. Then, the optimum oil content to maximum compaction could be specified.

Measuring oil recovery by weight accompanies errors in terms of water in oil (W/O) or oil in water (O/W) emulsions in thermal displacement processes. The samples from the reference test were centrifuged after gravitational separation. The error for the separation is around 0.2%, which is neglected in this study because of the low impact and the availability of the centrifuge. When a sandpack of a higher geometrical dimension was used, the quantity in W/O emulsions increased significantly.

The wettability of the sand grains is difficult to determine. In this experiment, the grains are in direct contact with the heavy oil since there is no initial water saturation. Furthermore, the water used in this study was tap water which was assumed to have a neutral pH and to have limited divalent ions impacting interfacial interactions.

Heat loss of to the overburden and steel core holder was minimized by insolating the coreholder with glass wool. It is assumed that the heat loss is consistent for the setup.

Chemicals. The steam additives should meet certain requirements to be applicable in the high temperature and pressure environment. Thermal stability is a major criterion in selecting a proper chemical for improving steam flooding. The operation temperature varies with the different method applied in the field and the quality of the steam. The chemical additive must remain in its original form while moving in the steam chamber until it reacts at the interface between steam and oil. Ideally, the chemical should vaporize together with water at similar temperatures and should condense at the chamber boundary, where latent heat transfer of the condensate can be improved (Mohammadzadeh et al., 2012). Table 2.1 provides an overview of the chemicals used in this study.

Determination of optimal application conditions requires detailed studies on the selected chemicals. This designed procedure is a comparative analysis to identify the incremental recovery mechanism each chemical but it is not designated to analyze and define sensitivity for distinct parameters, such as temperature limits, concentrations, formation water, etc. The experimental matrix would be too large considering the resources required to obtain the results. The concentration was equalized for all the chemicals to 2%wt. after starting the experiments with 1%wt. where no differences were observed. Pratama and Babadagli (2018) investigated the effect of temperature on wettability considering factors such as concentration of divalent ions and pressure. This methodology can be adapted to specify specific concentrations for the screened chemicals.

Surfactants are widely accepted as an enhanced oil recovery agent. It acts between surfaces to reduce interfacial tensions, change wettability, improve emulsification and create foam. Gupta and Zeidani (2013b) outlined the problem of the selection criteria for a suitable surfactant under field condition in a “surfactant-steam process” (SSP) and named the properties that a surfactant should possess: (1) Reduction of IFT, vaporizes at operation conditions, thermally stable at high temperatures (retain its properties and remain effective at high temperature); (2) emulsification

Table 2.1: Overview of the experiments conducted with the concentrations of the chemical additives and the injection points.

Nr.	**Chemical**	**Description**	**Concentration**
1	Reference	Upper limit confidence interval	–
		Anionic Surfactant	
2	O332	Internal Olefin Sulfonate	2 %wt.
3	LTS-18	Linear Alkyl Toluene Sulfonate	2 %wt.
		Non-Ionic Surfactant	
4	Tween 80	Polyoxyethylene sorbitan monooleate	2 %wt.
5	Tween 85	Polyoxyethylene sorbitan trioleate	2 %wt.
6	Span 80	Sorbitan monooleate	2 %wt.
7	Span 85	Sorbitan trioleate	2 %wt.
8	Triton X-100	Phenol Ethoxylates	2 %wt.
9	Novelfroth 190	Alcohol Ethoxylates	2 %wt.
		Ionic Liquid	
10	Ionic Liquid	BMMIM BF_4	2 %wt.
		High pH Solution	
11	Sodium Metaborate	$NaBO_2$	2 %wt.
		Solvent	
12	Heptane	C_7H_{16}	2 %wt.
13	Dimethyl Ether (DME)	C_2H_6O	2 %wt.
14	Biodiesel	Fatty acid methyl ester (FAME)	2 %wt.
		Nanoparticles	
15	Silicon Oxide	SiO_2	2 %wt.

(preferentially oil-in-water emulsion); (3) wettability alteration to more water-wet conditions; and (4) compatible with formation water.

Sulfonate and sulfate surfactants are known to be thermally stable until temperatures of 200-250°C from commercially available data. Especially the linear alkyl toluene sulfonate LTS-18 was considered for steam applications (Barnes et al., 2010; Buijse et al., 2010). The alcohol alkoxy sulfate (AAS) J11111, however, can retain its properties for up to 60°C reservoir condition and can be used as an additive for hot water injection. Tween, Span, Triton and Novelfroth are non-ionic surfactants.

Biodiesel (fatty acid methyl esters) was tested as a surfactant agent by Babadagli et al. (2010) and Babadagli and Ozum (2010). The visual comparison of the condensates led to the assumption that biodiesel condenses with the steam at high-temperature conditions.

Ionic Liquids are mainly studied for the separation processes of oil sand and bitumen. However, its capabilities in acting in as a surface agent between bitumen and sand. Hogshead et al. (2011) investigated with an atomic force microscopie (AFM) the forces between bitumen and silica with 1-butyl-2,3-dimethyl-imidazolium tetrafluoroborate ([BMMIM BF_4]) and observed a reduction in adhesion by using the ionic liquid. Also, Wei and Babadagli (2016, 2017) proved the wettability modification of BMMIM BF_4 to a less oil-wet surface at different temperatures (25°C, 90°C, and 180°C) and the improvement of gravity force by the chemical agent sodium metaborate ($NaBO_2$). The surface activities of the ionic liquid and the high pH solution might have an influence in gravity-driven flow regimes.

Nanoparticles or nanofluids are new generation fluids with nanoscale colloidal suspensions containing condensed nanomaterial. The enhances thermophysical properties, such as thermal diffusivity and conductivity, is one function of the nanoparticles which is one of the key functions in enhancing thermal gravity drainage (Yu and Xie, 2012). In this study, the nanofluid silicon oxide was used. Alomair et al. (2014) conducted research on SiO2 and its application in heavy oil recovery and showed that a reduction in interfacial tension is possible to eventually generate emulsion.

Sheng et al. (2017b) reported a comparison of a water-soluble solvent, dimethyl ether (DME), with butane in a simulation study. The results showed that DME can be promising in reducing SOR by 35% with an increase of 8% in ultimate recovery. DME is the only chemical in this study that is naturally in the gas phase. The setup was modified by using an ISCO pump to inject the DME into the coreholder with a low pressure.

2.4 Results and Discussion

The experiment conducted in this study can be separated into the two categories: Reference (steam only) and co-injection of additives. To obtain a comparable result, water was injected into the core instead of the chemical solution. A summary of the results is outlined in Table 2.1.

Thermal Stability. Thermogravimetric analysis (TGA) were conducted for the listed chemicals and the results are shown in Figure 2.2.

A TGA measures the weight loss over temeprature increase at a certain heating rate. 15mg of chemical were tested under a heating rate of $15°C/min$. This test provides quantification of chemical decomposition of selected chemicals for high temperature application and can be used as a thermal stability test. A few of the chemicals (namely SiO_2, $NaBO_2$ and Ionic Liquid) were tested by Wei and Babadagli (2017) and are added to this Figure. A disadvantage for this method of measuring thermal stability is the exposure to elevated temperature for a long time.

The mass for the non-ionic surfactant is for almost all chemicals consistent over increasing temperature. Igepal CO-890, a polyoxyethylene nonyl phenyl ether, and Tween80 start to drop in mass at around 250°C. Igepal is in the solid phase which prevents the testing of this chemical

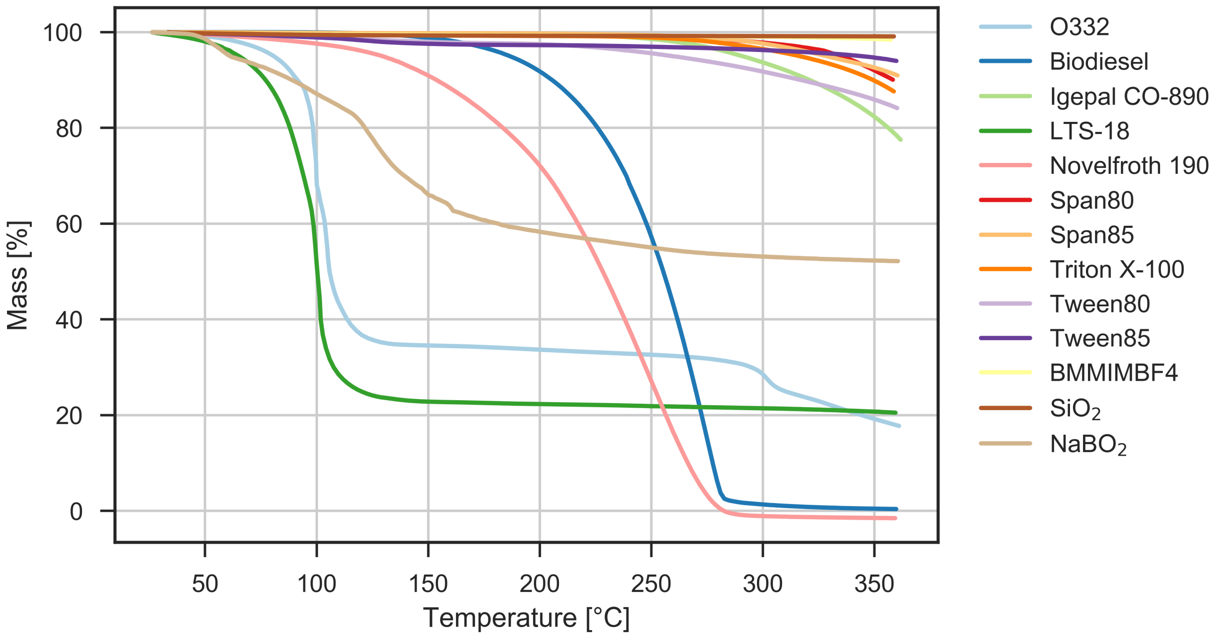


Figure 2.2: Thermogravimetric Analysis (TGA) for the selected chemicals in Table 2.1 representing mass loss over increasing temperature. The heating rate was $15°C/min$.

with this methodology since a high viscous liquid would need to be injected. Tween85 is a tri-ester product and exhibit better thermal stability than the mono-ester comparative Tween80 most likely due to the higher molecular weight. However, Span80 as sorbitan monooleate shows similar decomposition compared to the sorbitan trioleate Span85. For the anionic surfactants LTS-18 (Linear Toluene Sulfonate, LTS) and O332 (Internal Olefin Sulfonate, IOS), mass loss occurs already in the initial stage of the TGA. At around 100°C, the masses of both chemicals drastically drop to 20% for the LTS and around 30% for the IOS. This can be explained by a potential dehydration reaction. A similar reaction was measured for sodium metaborate by Wei and Babadagli (2017) where a theoretical content of 52.25%wt. of water was reported. Biodiesel and Novelfroth 190 decompose completely at a temperature of around 270°C which is out of the temperature range applied in this study. Very good stability can be concluded for the nanoparticle SiO_2 and ionic liquid where no mass loss is observed.

Reference test. In the first part of this experimental study, the calibration and validation of the system was achieved by conducting reference tests with steam only. Figure 2.3 shows the pressure and temperature data recorded during the reference tests.

It can be observed that the outlet temperature and pressure differential exhibit a non-monotonic behaviour. When these parameters reached a local maximum, oil and condensate were produced

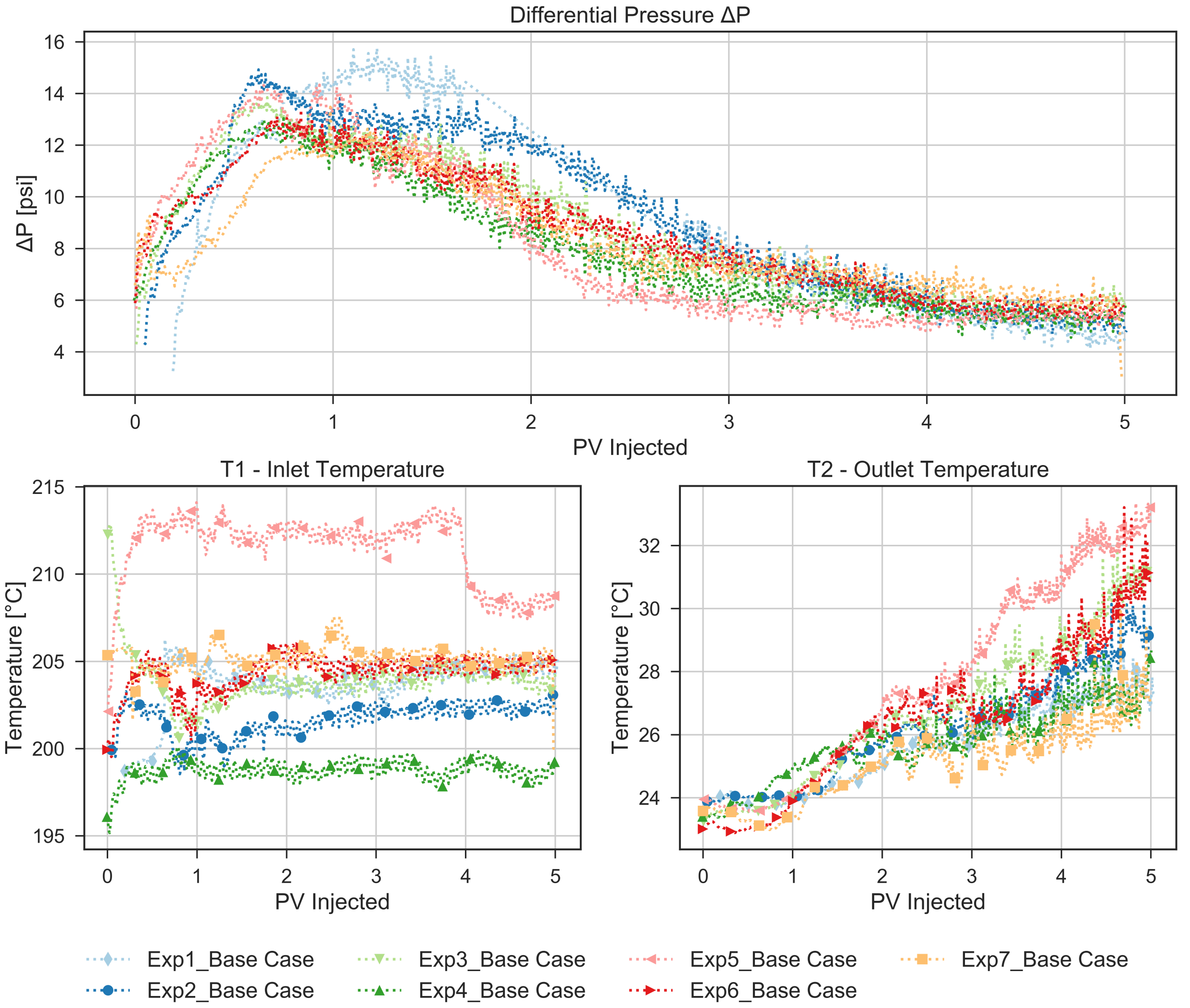


Figure 2.3: Pressure (top) and Temperature (bottom) profile of the reference test with only steam and oil.

after 1 PV injected, which led to a decrease in differential pressure and an increase in outlet temperature. The pressure difference is kept small over the time (6-16 psi). The increase in outlet temperature shows a linear relation. The heat transferred into the sandpack is strongly dependent on the inlet temperature. Experiment 5 deviates from the other reference tests with a higher inlet temperature T1 (around 10°C) and yielded in the highest outlet temperature T2 with around 33°C. In this study, the T2 and ΔP curves were regressed to calculate the coefficient of determination (R^2) and to enhance confidence in the evaluation. The results are depicted in Figure A.5 in the Appendix. The oil recoveries of the repeated reference tests are shown in Figure 2.4.

A total of seven experiments were conducted to generate the data for interpreting trend and deviations statistically. A similar trend and ultimate recovery can be observed in Figure 2.4 which is also proven with the high R^2 of 0.9539. The experiments are normalized over pore volumes

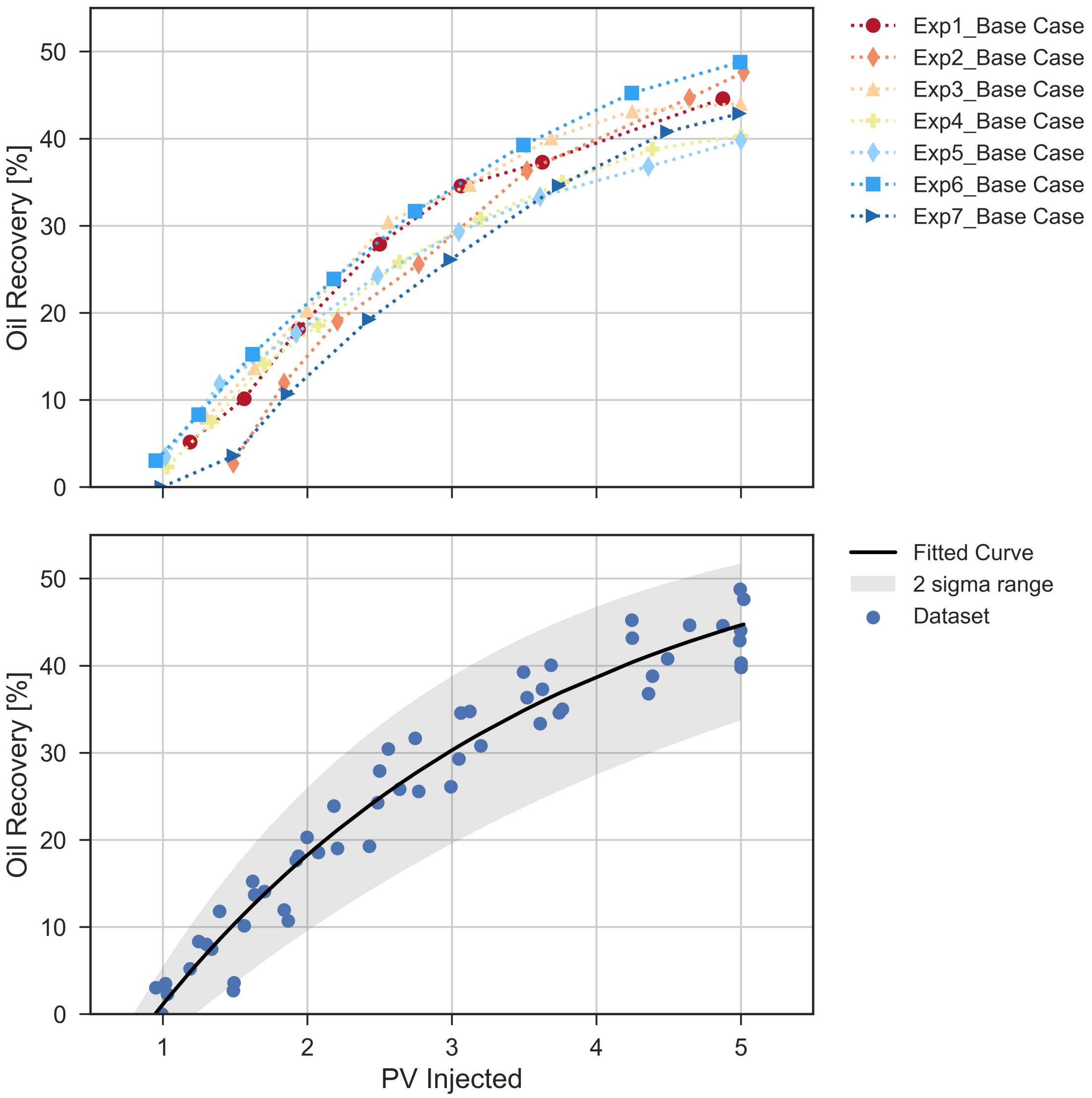


Figure 2.4: Summary of the oil recoveries of the reference tests conducted normalized over pore volumes (PV) injected.

(PV) injected to evaluate oil recovery between the experiments. Furthermore, the normalization fixes the total steam injected to focus on the produced oil impacting steam-oil ratio (SOR). The ultimate recoveries of the experiments range from 40-50% after 5 PV water injected. For the interpretation of the injected chemicals, a confidence band of a two sigma (95%, grey area, Figure 2.4) range was calculated for the fitted function to exclude any experimental errors. A positive effect of a chemical is attributed to the oil recovery being outside and above of this interval.

Interpretation of Flow Pattern. In this setup, a high quantity of water was injected (5 PV) to reach the designated ultimate recovery. This can be explained by the high mobility difference between the heavy oil and the displacing steam. The flow pattern of the steam is shown in Figure 2.5. Distance rings on the top and bottom (Figure 2.1) maximize the exposure of steam to the top of the core sample to avoid a single stream entering. However, the steam bypasses along the outside of the core where permeability is assumed to be higher due to packing discontinuity. This causes the drainage of an oil-condensate mixture and a downward expansion of the steam chamber. A core was extracted from the sleeve (right, Figure 2.5) in an experiment using a bigger sample to prove these interpretations. The colour change from the top to the bottom can be seen clearly as well as the bright brown sand grains at the outside of the core.

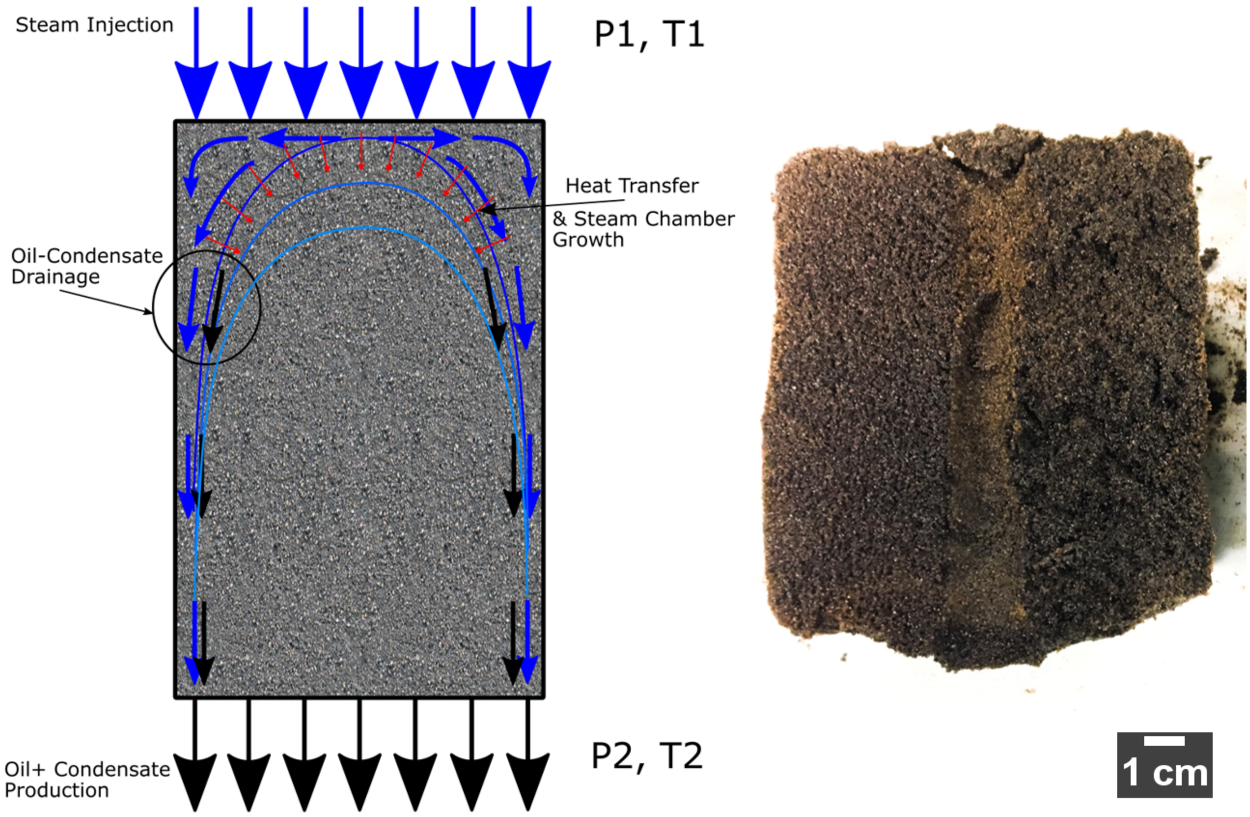


Figure 2.5: Interpretation of flow pattern in the core sample.

Co-injection. The ineffectiveness of the chemical injection in the tertiary stage (description of tests in Appendix) led the study to focus on the co-injection of additives beginning at 1 PV injected of the experiment. The experiments can be categorized into anionic and non-ionic surfactants, an ionic liquid, a high pH solution, solvents and a nanoparticle (Table 2.1). Table 2.2 shows the results of the experiments based on the performance in SOR. The produced liquids were always observed for emulsification or other effects with the blind eye. In the following, the results are described in detail with possible assumptions of mechanisms involved in impacting increment in oil recovery. Figure 2.6 illustrates the recovery curves of the experiments with the calculated confidence interval of 95%.

Table 2.2: Overview and comparison of the results in ultimate recovery.

Nr.	**Chemical**	**Ultimate Recovery**	**Increase Recovery**	Ranking
1	Reference	51%	–	–
		Anionic Surfactant		
2	O332	39.49%	–	–
3	LTS-18	53.84%	2.84%	8
		Non-Ionic Surfactant		
4	Tween 80	55.54%	4.54%	5
5	Tween 85	48.76%	–	–
6	Span 80	58.07%	7.07%	4
7	Span 85	44.49%	–	–
8	Triton X-100	48.76%	–	–
9	Novelfroth 190	54.93%	3.83%	6
		Ionic Liquid		
10	Ionic Liquid	54.45%	3.5%	7
		High pH Solution		
11	Sodium Metaborate	46.82%	–	–
		Solvent		
12	Heptane	62.01%	11.01%	1
13	Dimethyl Ether (DME)	46.53%	–	–
14	Biodiesel	58.43%	7.43%	3
		Nanoparticles		
15	Silicon Oxide	60.32%	9.32%	2

Nonionic Surfactants. Common non-ionic surfactants are based on ethylene oxide, which are referred to as ethoxylated surfactants (Tadros, 2013b). The net charge of a non-ionic surfactant is neutral opposing to anionic (negative charge) and cationic (positive charge) surfactants. A major advantage for non-ionic surfactants is the water-solubility and the increased surface activity in high-temperature environments. Non-ionic surfactants are also stable over a wide range of pH. This study selected phenol and alcohol ethoxylates (Triton X-100 and Novelfroth 190, respectively), fatty acid esters of sorbitan (Span) with the ethoxylated products polyoxyethylene sorbitan (Tween) as representatives for non-ionic surfactants. Novelfroth 190 exhibited mass reduction with increasing temperature as an only non-ionic surfactant (Figure 2.2). Despite the result obtained from the TGA, the tested alcohol ethoxylate increased the oil recovery by 4% measuring from the upper boundary of the confidence interval. Potentially, the optimal operating temperature of an alcohol ethoxylate was matched with the temperature distribution in the core flood. Complete mass loss (0%) can be observed at a temperature of around 270°C, which is 70°C

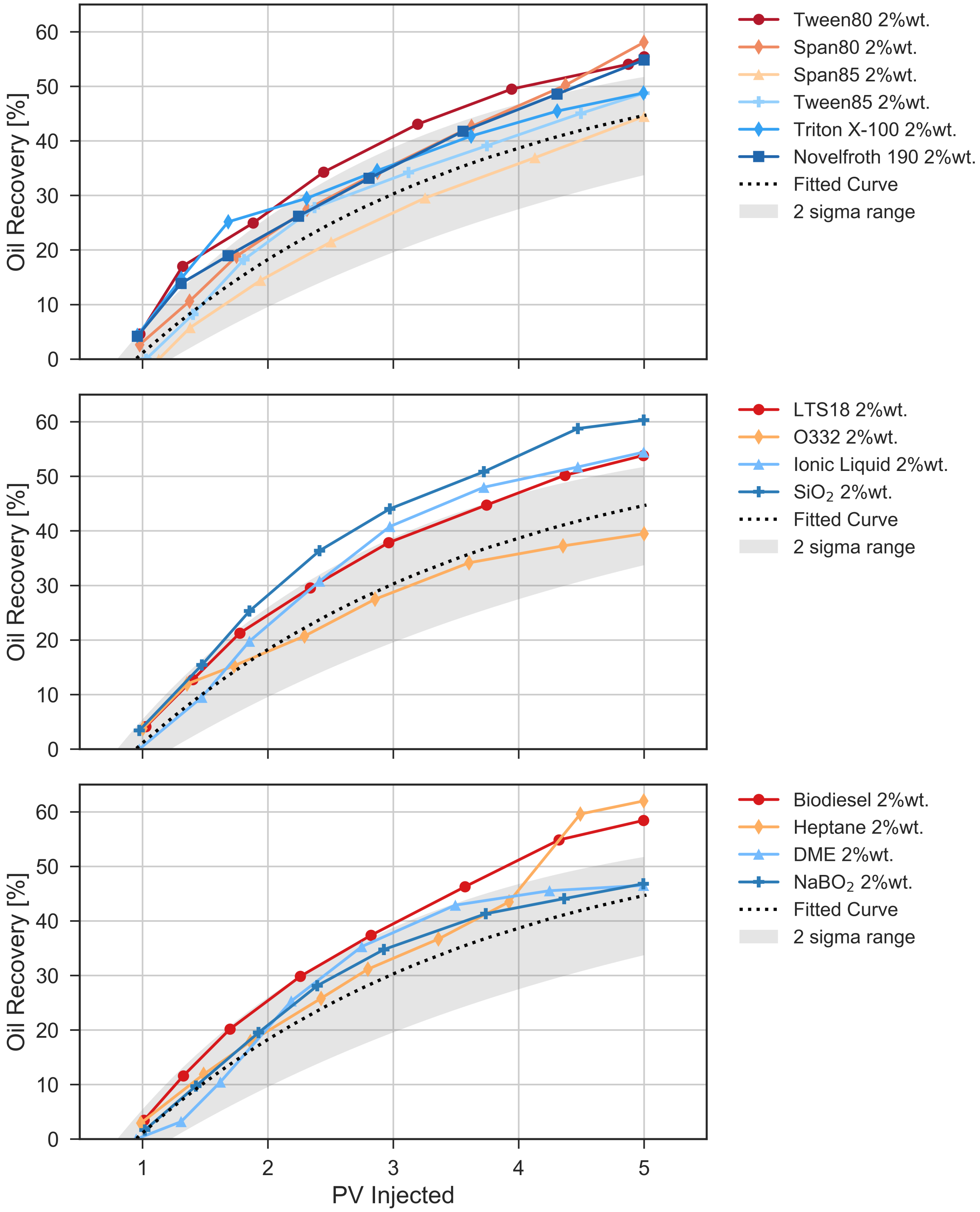


Figure 2.6: Recovery curves of the experiments injecting an equalized concentration starting from 1 PV.

higher than the injection temperature. Based on the manufacturer's documents, the boiling point for the ethoxylated alcohol is 166°C which means the chemical was injected in the gaseous phase. It can be noticed that the majority of the test samples were measured in the range of the CI. The shape of the recovery curve indicates a linear inclination after around two PV injected without an indication of declination with higher PV injected. A similar trend can be observed with the sorbitan monooleate, Span80. Sorbitan monooleate ($C_{24}H_{44}O_6$) led to an increase of 7% and was the best non-ionic surfactant out of all the candidates (Figure 2.6). It should be taken care with this interpretation as Span80 has a high hydrophilic-lipophilic balance (HLB) value of around 4.5 and, hence, promotes water in oil (W/O) emulsions. On the other hand, the ethoxylated derivates (here Tween80) with a high HLB value of around 15.0 showed good performance in oil recovery by an increment of 4.5%. The improved water solubility was monitored by the colour change when the water was separated from the produced oil (Figure A.1). The tri-ester subcategories Tween85 and Span85 indicated that a higher esterification is not efficient in improving oil and condensate drainage. Further on, Triton X-100 as a representative for a phenol ethoxylate did not improve oil recovery. Similar to the Tween80, a colour change in produced water phase was observed with a small quantity of oil droplets (Figure A.1). It should be noted, that the O/W emulsions was significantly low and did not make a great impact in ultimate. The enrichment at the oil-water interface (surface excess concentration) requires further investigation since the produced surfactant was not quantified. IFT measurements at a constant temperature with increase in concentration are recommended to specify the maximum decrease in surface/interfacial tension (critical micelle concentration (CMC)). Summarizing this, sorbitan based surfactants, such as Span and Tween, can be very effective in steam applications.

Anionic Surfactants. Two sulfonates, LTS-18 and O332, were tested with the methodology of injecting with a slow flow rate the cold chemical into the tubing. Both of the chemicals showed drastic weight loss at around 100% to 20-30% of the original mass. While injecting the LTS-18, the dehydration of the chemical left a very thick residual behind. This caused plugging of the channel for the chemical at the near end of the experiment, after 89% of the concentration was injected. However, an increase in oil recovery of around 3% can be noticed to the upper boundary of the confidence interval (CI) (Figure 2.6). It is believed that a major contribution to the improved efficiency was the result of pore plugging of the injected LTS. The majority of the concentration was introduced into the sandpack, where it dehydrated due to the increasing temperature. The blockage of the swept regions opened new paths for the steam/condensate to displace the heavy oil. When tested in the preliminary study with a high-pressure steam, LTS-18 had the highest oil recovery with a 33% increase to the reference case (Figure A.4).

Ionic Liquid. The interfacial activity of the selected ionic liquid and the excellent thermal stability was already proven in the literature (Hogshead et al. 2011, Wei and Babadagli 2016, 2017). The major contribution of ionic liquid was reported to be a wettability modifier to a more water wet state which is specifically for steam applications preferable. In this experimental study, the ionic liquid enhanced the oil recovery by 3.5% after injecting 2%wt. of concentration into the sandpack (Figure 2.6). As previously explained, the oil is in direct contact with the sand grains and aged for 24 hrs assuming a preferably oil-wet affinity. The ionic liquid may have altered the wettability of the sand grains to a water-wet state, as it was also reported by Wei and Babadagli (2016, 2017). Considering the proven reduction of adhesion energy by Hogshead et al. (2011) in the separation process of bitumen and matching it with this results, an ionic liquid may be a very successful candidate for potential in-situ field application.

Nanoparticle SiO_2. A novel research area of improving oil recovery is the utilization of nanotechnology specifically nanoparticles to solve issues related to conventional mechanisms. This study used silicon oxide as nanomaterial which was dispersed in water with 25%wt. The size of the particles ranges from 5-35nm. Oil sands consist of a high quantity of quartz which is composed of silicon and oxygen atoms. Therefore, injecting silicon oxide would imply environmental friendliness as original minerals are employed (Sun et al., 2017b). Strong attractive forces between the particles can cause agglomeration and, thus, transportation challenges through the wellbore and/or in porous media. This issue was also observed in this experiment, where the suspended nanomaterial agglomerated inside the tubing. The aqueous suspending phase (in this case water) vaporized whereas the nanoparticles deposited and plugged the tubing. Change in inside diameter of the tubing did not improve this drawback after the test was repeated multiple times. Based on these results, the concentration of the nanofluid was spread on top of the sandpack simulating a start-up injection of a nanoparticle solution before the injecting the displacing steam phase. This procedure yielded an improved oil recovery of around 9% and ranked as the second most efficient chemical in SOR. In the first set of experiments, the nanoparticle accelerated the production, which can be attributed to its positive effect on oil/condensate drainage due to the Pickering emulsions.

Biodiesel. A fatty acid methyl ester (FAME) shows amphiphilic molecule properties with its hydrophobic hydrocarbon chain (C_nH_m; $m < 2n + 1$) and the ester with a methyl group as hydrophilic part (-COOCH3) (Babadagli et al., 2010; Babadagli and Ozum, 2010). The injection of a biodiesel led to an increase in oil recovery by 7.4%. The injection of a biodiesel achieved also the second highest recovery (67%) with the first attempts of high-pressure steam injection (FigureA.4). The mechanics of a biodiesel\condensate\bitumen system are still unclear. Babadagli and Ozum (2010) emphasized concerns related to the solubility of biodiesel in bitumen which can be controlled by the diffusivity coefficient and the steam-bitumen surface area. Nevertheless, the incremental oil recovery could be the diffused biodiesel into the oil phase. The interfacial activities and mixing behaviour of fatty acid methyl ester or derivatives need to be further investigated.

Solvents - Heptane and DME. Solvents were used to dissolve into the oil phase to change the composition and improve flow behaviour with a change in specific parameters, such as viscosity and mobility difference. Heptane was selected as a hydrocarbon solvent and increased the recovery by 11% which ranks as the most efficient chemical in SOR. The recovery increased at the end of the experiment which indicates the diffusion of heptane into the oil phase. This late recovery increase can be seen by the refractive index measurements of the samples (Appendix Figure A.6). Based on this measurement the retrieved heptane was around 35.29%. Heptane, as an alkene solvent, triggers asphaltene precipitation due to the insolubility. Therefore, SARA tests using samples taken from the core flood with different concentrations of heptane were conducted and analyzed. The results of the reference test, heptane 1%wt. and heptane 5%wt. are shown in the Appendix Figures A.7. The samples were taken at distinct times during the progression of the experiment (Sample#1: beginning, Sample#5: end). The asphaltene content decreases significantly to 15% and 13% in the 1%wt. and 5%wt heptane experiment whereas the resins fraction increases to around 30-35%. Asphaltene molecules are suspended and stabilized by the resins in the crude oil (Ahmadi et al., 2014; Hammami et al., 2000). The injection of miscible gas or a light paraffinic solvent changes the solubility of the asphaltene component in the oil phase. Therefore, the equilibrium between the asphaltenes and resins is disturbed and the resin component desorbs from the asphaltene surface in order to reestablish the thermodynamic equilibrium. This causes an increase in surface free energy of the asphaltene micelles which initiate agglomeration to reduce the energy potential and separate as a solid phase. Then, the produced oil phase has a higher content of resins and a lower content in asphaltenes which is clearly proven with the conducted SARA analysis. Further on, viscosity decreases with the precipitation of asphaltene as a heavy component in the oil and promote improvements in mobility control. The water-soluble solvent DME was injected in the gaseous phase but did not achieve an enhancement in SOR.

2.5 Economical evaluation

Applying enhanced oil recovery methods is only feasible considering the cost involved in the improvement of the return factors, such as SOR. The cost ranking of the chemicals selected for the initial injection is depicted in Table 2.3.

Table 2.3: Overview of the prices for the selected chemicals

Nr.	**Chemical**	Ranking SOR	Commercial Price (CAD)	Price (CAD) equalized for 2%wt	Ranking Price
1	Reference	–	–	–	–
	Anionic Surfactant				
2	O332	–	–***	–	–
3	LTS-18	8	–***	–	–
	Non-Ionic Surfactant				
4	Tween 80	5	50.40 (/500ml)	0.75	4
5	Tween 85	–	75 (/500ml)	1.17	7
6	Span 80	4	55.4 (/250ml)	1.79	8
7	Span 85	–	54 (/250ml)	1.82	9
8	Triton X-100	–	54.4 (/500ml)	0.82	5
9	Novelfroth 190	6	–***	–	–
	Ionic Liquid				
10	Ionic Liquid	7	284.2 (/25g)	90.94	11
	High pH Solution				
11	Sodium Metaborate	–	54.4 (/500g)	0.87	6
	Solvent				
12	Heptane	1	746.15 (/20L)	0.44	2
13	Dimethyl Ether (DME)	–	545.15 (/20lb)*	0.48	3
14	Biodiesel	3	2 (/1kg)***	0.02	1
	Nanoparticles				
15	Silicon Oxide	2	64.68/120ml**	4.31	10

* Price of compressed gas
** 25%wt. nanofluid suspended in an aqueous solution
*** Prices not commercially available

The chemical prices were researched for the commercially available products and normalized to the same weight injected (2%wt.) to ensure comparison. It should be noted, that some of the chemicals are only available in the solid phase (ionic liquid, sodium metaborate) or gas phase (DME). Further on, this overview gives an idea of a price comparison and should not deal as a detailed economic evaluation. Some of the chemicals were donated and the prices were not published.

Heptane and biodiesel are cost effective and can be considered as the best performing chemical for steam applications in this screening study including parameters of cost and SOR. Non-ionic surfactants show similar prices, excluding Span80 and Span85, of 50-60 CAD for 500 ml. Based on the oil recovery results, Span80 is the most efficient surfactant for high-temperature application and, in contrast, the most expensive one with a price two times higher than other candidates, such as Tween80. Despite the good results in the initial and tertiary injection, the ionic liquid is the most expensive chemical that was tested. The water-soluble solvent DME is one of the cheapest chemical available from the presented chemical database. The designed methodology for this study was not meant to inject a chemical in the gaseous phase. To support promising results published by Sheng et al. (2017b), it is suggested to focus on a high-pressure steam injection in combination with the DME or to focus more on other water-soluble solvents as it is a very cost-effective solution to improve steam injection projects.

2.6 Conclusions and Remarks

Sandpack experiments with heavy oil were conducted to simulate steam flow in a porous media. Improvements of the flow characteristics were investigated using different chemicals at the same concentration of 2%wt., such as anionic surfactants (O332, LTS-18), non-ionic surfactants (Tween, Span, Triton, Novelfroth), biodiesel, ionic liquid (BMMIM BF_4), high pH solution ($NaBO_2$), solvents (heptane, DME), and a nanoparticle (SiO_2). The oil recoveries with the chemical prices were compared and evaluated. The following conclusions can be made:

1. Heptane was the most successful chemical to improve SOR by increasing the oil recovery by 11% if it is added at the beginning of the process. It is one of the cheapest chemicals of the products tested in this research. Asphaltene precipitation was proven as a supporting mechanism by conducting SARA analysis. A water-soluble solvent, DME, did not enhance oil recovery significantly.
2. Biodiesel could increase oil recovery by 7.43% yielding the third lowest steam to oil ratio. Further research is suggested to identify the contributing mechanisms of biodiesel as the diffusivity was not considered in this study.
3. From the anionic surfactants tested, the chemical agent LTS-18, a linear toluene sulfonate, is a promising surfactant in the application of steam injection with the 8th highest ultimate recovery with a 3% increase. However, degradation of the surfactant caused plugging of the tubing in the late stage of the experiment and is a theoretical mechanism to improve sweep efficiency by plugging pore space.
4. The non-ionic surfactants Span80, Tween80 and Novelfroth190 are suitable candidates for steam injection processes with their thermal stability and an upgraded SOR. However, using non-ionic surfactants may not improve the overall feasibility of a steam injection project considering the average prices of surfactants.

5. Ionic liquid showed a high efficiency at the tertiary steam injection stage with a temperature of 150°C as well as with the initial injection into the coreholder where an increment in oil recovery of 20% and 3.5% was achieved, respectively. Nevertheless, the ionic liquid used was the most expensive chemical from the product matrix.
6. A nanoparticle, SiO_2, was dispersed in water but injectivity problems were observed due to vaporization of water and the aggregation of the particles. The nanoparticle was then placed initially in the sandpack and could improve the oil production by 9.32% which ranks this experiment as second lowest SOR. However, the purchased nanofluid is the second most expensive chemical measured by the available, commercial prices.

Chapter 3

Recovery Improvement by Chemical Additives to Steam Injection: Identifying Underlying Mechanisms through Core and Visual Experiments

This paper is a revised and modified version of the paper SPE-190083 presented at the SPE Western Regional Meeting held in Garden Grove, California, USA, 22-27 April 2018.

3.1 Preface

Steam injection of any kind (flooding, cyclic, or gravity drainage) is a proven heavy-oil recovery method; however, it also involves excessive costs due energy and water needed for steam generation. Any effort in reducing this cost or improving oil recovery is essential for sustainable production, especially in times of low oil prices. Chemical additives to steam were suggested a few decades ago to improve two major mechanisms, namely heat transfer and interfacial phenomena, but research in that area discontinued due to the cost and thermal stability problem of the additive chemicals. With recent advancements in nano-technologies, new generation chemicals showed potential to reconsider chemical additives to improve the efficiency of steam injection. This, however, requires extensive research especially for mechanism identification. The objective of this paper is to identify the flow characteristics and the mechanisms involved in recovery enhancement by chemical additives through core and visual tests.

To mimic the gravity assisted drainage and flooding type steam displacement tests we performed previously (Bruns and Babadagli, 2017) on cores saturated with 27,000 heavy-crude-oil, a visual Hele-Shaw model was designed to simulate the same process and identify the physical characteristics of the steam-condensate-oil interface and the role played by added chemicals. Majority of the chemicals/chemical blends showed either improvement in the rate or ultimate recoveries in the coreflooding tests and, based on this data, the best performing and the most thermally stable chemicals were selected for the visual tests. These chemicals include ionic liquids, anionic surfactant (linear toluene sulfonate), non-ionic surfactants, biodiesel (thermally stable surface active agents) and solvents (heptane), and nano-fluids (silicon oxide). The chemical solution was injected at constant rate and pressure after being vaporized in an oven along with steam and the whole process was recorded with a camera.

The contribution to recovery improvement through these phenomena in flooding and gravity controlled cases were identified. Foaming, emulsification, and IFT reduction yielding reduced drag forces between two phases at the interface were observed to be the main reason for positive contribution of chemicals. Biodiesel exhibited a diffusion-like behavior near the injection port where no residual oil was noticed. The solvent (heptane), simulating ES-SAGD, stabilized the flow of steam in the late stage of the experiment due to the viscosity reduction. Improved oil + condensate drainage was assumed to be the contributing mechanism because of the change in surface properties during the injection of the ionic liquid. Nanoparticle, silicon oxide, and the linear toluene sulfonate (LTS) showed similar improvements in tip-splitting of the displacing fingers. It was concluded that the interfacial tension (IFT) reduction resulted in a wider occupation of the Hele-Shaw cell (better lateral sweep). Non-ionic surfactants showed different emulsion capabilities and high efficiency in steam/condensate displacement with a higher HLB (hydrophile - lipophile balance) value.

Keywords: Steam additives, surfactants, nanofluids, gravity and viscous displacement, visual 2D experiments

3.2 Introduction

Steam injection is a promising and efficient thermal recovery method where heat is transferred from the injected steam into the cold heavy oil phase to mobilize it by decreasing viscosity. However, high energy consumption by steam generation with excessive CO2 emission and costly post-production water treatment have directed a research path towards the combination of thermal and chemical enhanced oil recovery techniques (Al-Bahlani and Babadagli, 2009; Deng, 2005) especially for energy-intensive steam assisted gravity drainage (SAGD) applications. As stated in a comprehensive review by Al-Bahlani and Babadagli (2009), several drawbacks with a lack of knowledge on the physics of the SAGD process entail detailed analyses to improve its efficiency.

Examinations of processes involving high temperature and pressure applications, such as SAGD or cyclic steam stimulation (CSS) accompany high complexity in visual experimental design, accuracy, and execution at the laboratory conditions. Visual models such as Hele-Shaw cells and micro-models with specifically-designed pore geometries are commonly used to visualize flow behaviors at different physical conditions, especially interface propagation and interaction between fluids during displacement processes.

A Hele-Shaw cell gives an approximation of the fluid flow between two parallel flat plates separated by a small gap. This setup was used in a pioneer papers by Chuoke et al. (1959) and Saffman and Taylor (1958), which dealt with the stability analysis of a displacing fluid with less viscosity to the pore filling fluid in a porous medium. Starting with the Navier-Stokes equation, the flow through a thin gap of thickness b and a vertical placed Hele-Shaw model can be simplified to:

$$u = -\frac{b^2}{12\mu} \bigtriangledown (P + \rho g z) \tag{3.1}$$

with the assumptions of a single-phase, incompressible flow ($\bigtriangledown u = 0$) with low Reynolds number (Re << 1). Therefore, the governing equations of the Hele-Shaw flow match the empirical relation describing fluid motion in a porous medium (Darcy's law).

Kong et al. (1992) published the first noteworthy paper using a Hele-Shaw cell to examine the transport phenomena of several types of oil (Newtonian and non-Newtonian behavior) by steam with horizontal and vertical flow directions. The authors outlined that heat loss through the exposed glass is not controlled by insulation or other equipment. It was assumed that the heat loss would not affect the interface advancement and claimed to be verified in sensitivity experiments (Kong et al., 1992). This paper compares and validates these results of fluid motion including excessive heat loss with differences in insulation by an applied vacuum in a chamber.

In another pioneering study, Mohammadzadeh and Chatzis (2010) conducted pore scale experiments and investigated specific mechanics of gravity drainage in a Hele-Shaw model with homogeneous, etched porous patterns. Special focus was placed on the major contributions for gravitational drainage processes, which included immiscible displacement of heavy oil by steam, development of residual oil saturation as well as micro-scale emulsification. Later, Argüelles-Vivas and Babadagli (2016) performed pore scale visual experiments to identify the causes of residual oil saturation behind the steam chamber during SAGD processes.

Addition of chemicals to the steam phase to improve the efficiency of steam applications make the process' control and experimental design even more complex. Before detailed pore scale and visual analysis for the effects of chemicals on the recovery improvement, suitable chemicals need to be selected. At elevated temperatures, decomposition or thermal stability is one of the major parameters contributing to the adaptability of chemicals for steam operations. In two consecutive studies by Wei and Babadagli (2016, 2017) and Cao et al. (2015, 2017), chemicals were already selected by analyzing static experiments in high temperature environments, such as imbibition/drainage tests, contact angle, interfacial tension (IFT) measurement, and Thermalgravimetric Analysis (TGA) to quantify thermal stability. Promising results were obtained from an ionic liquid, a high pH solution (sodium metaborate, $NaBO_2$), and a nanofluid (zirconium oxide, ZaO_2).

In our previous work (Bruns and Babadagli, 2017), these chemicals were validated together with different surfactants, a solvents (heptane), and a nanoparticle (silicon oxide, SiO_2) by an injection of the steam additive in core flood experiments. The conclusions based on these experiments are taken into consideration for this study to identify certain mechanisms that caused high deviations in the recovery curves. The next step is to clarify the role of these additive chemicals on the steam recovery improvement using visual data. This paper presents the initial observations obtained from the Hele Shaw version of the previous coreflood tests presented by Bruns and Babadagli (2017).

3.3 Experimental Materials and Methodology

A Hele-Shaw model was designed to visualize and explain different effects of selected chemicals on the steam performance when used as additive. The observations of emulsification, steam fingering/sweep efficiency, and oil film left behind the steam interface were evaluated by comparing the images acquired with the “blind eye”.

Materials

The Hele-Shaw cell, made of two plexiglass plates and a rubber sleeve in between with the dimensions of 10 cm wide x 15 cm length was fixed and sealed by two stainless steel frames. The best result of visualizing steam flow was found to be at a clearance of 0.5 mm. The cell was saturated with a heavy crude oil with a viscosity of 27,000 cp and a density of 0.99 $[g/cm^3]$ at 21°C. Rheology measurements showed a linear relation between shear rate and shear stress and, therefore, a Newtonian behavior of the oil.

Setup and Procedure

The Hele-Shaw setup was designed analogous to the etched glass and glass bead experiments conducted by Mohammadzadeh and Chatzis (2010) and Argüelles-Vivas and Babadagli (2016), respectively. The schematic is shown in Figure 3.1.

Water was injected into a container by an Isco Pump inside an oven. The oven temperature was set to 200°C. The band heaters along the tubing ensured prevention of heat loss and a guaranteed injection of saturated steam. After a pre-heating phase of one hour, where steam was circulated through the system, the steam phase was examined for the brightness with a dark background to confirm minimum injection of water droplets. A large exposed surface area of the cell would cause high heat loss and most likely an injection of hot water instead of saturated steam. A vacuum chamber surrounding the model was included to avoid such drawbacks in this experimental design of the Hele-Shaw model as suggested by Mohammadzadeh and Chatzis (2010) and Argüelles-Vivas and Babadagli (2016). An infrared camera (16x4 grid) was installed to validate readings from thermocouples and to visualize the temperature profile of the moving interfaces. Pictures were taken in pre-defined periods and two pore volumes (PV) of steam were injected in total. The inflow of the steam occurred naturally and was not forced by the pump due to the atmospheric condition and the low flow rate. Therefore, the flow of “free-fall gravity drainage” as well as natural steam channeling can be validated because of low pressure differential and viscous forces. The cold chemical was injected with a syringe or accumulator at certain times and the phase change was conducted by mixing with the steam phase. The experiments were repeated to validate the monitored effects

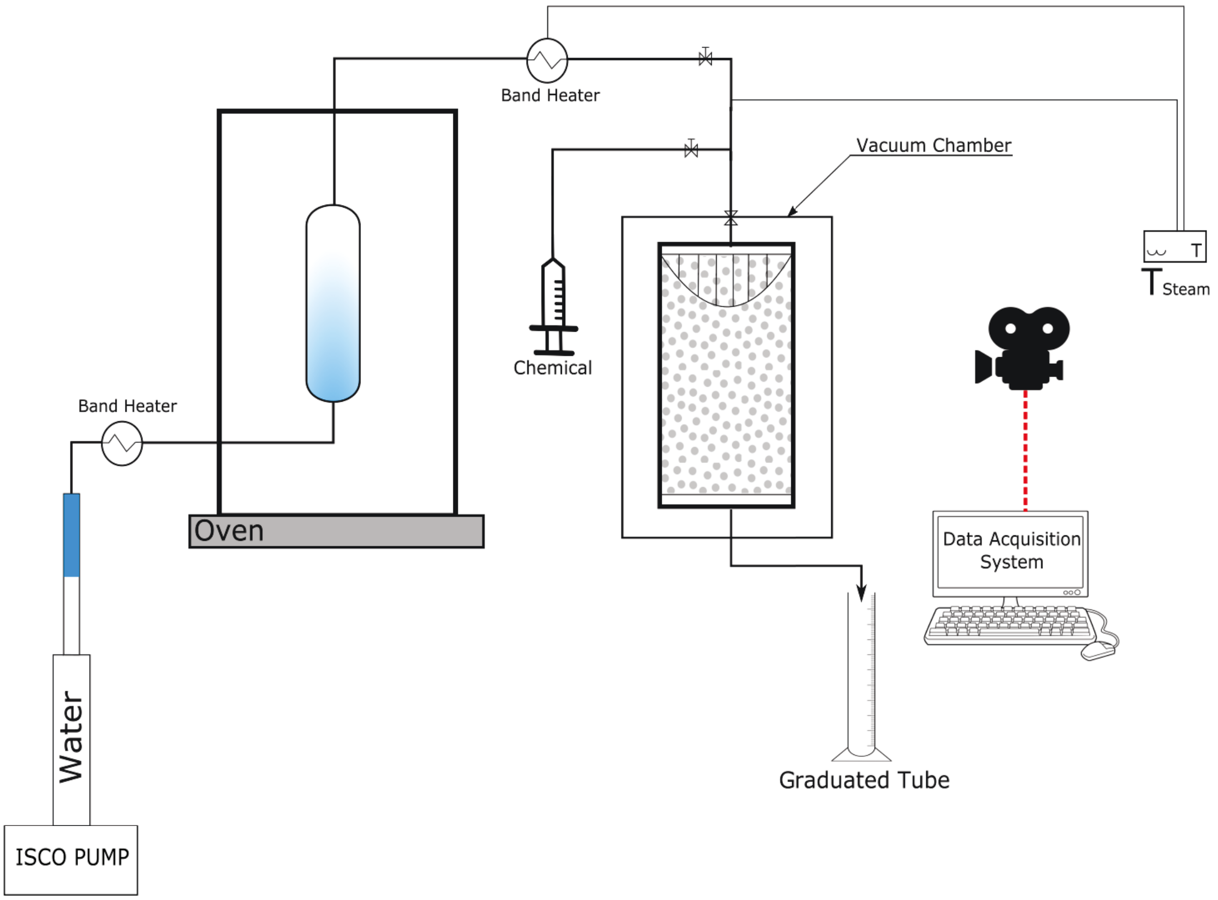


Figure 3.1: Design of Steam Displacement in a Hele-Shaw Cell.

of the used chemicals.

Two different sets of experiments were conducted in which the displacement of steam/condensate was evaluated with and without an excessive heat loss and with different placement of injection and production ports. The full chemical concentration was injected into the system at the beginning in the first set (**SET 1**). The goal was to observe the effects at the propagating interface where unstable displacement with strong steam fingering should occur in the initial stage (Kong et al., 1992). Then, steam was injected with a constant rate of 0.1 ml/min.

In the second set (**SET 2**), pressurized steam was injected with a constant pressure depletion rate from the side to visualize steam chamber growth with impact of buoyancy forces. The pure chemical was then introduced into the system with a defined rate. These experiments were operated with a vacuum to display anticipated improvements in heat transfer of the steam into the cold heavy oil.

Setup and Procedure

Different types of chemical additives to steam have been studied to enhance oil production since the 1980s. A comprehensive review of field tests operated with surfactant as additional injection component is given by Castanier and Brigham (1991). Followed by the potential drawbacks in the application of steam or thermal flow mechanisms, such as high water-cut and high operating costs (Al-Bahlani and Babadagli, 2009; Singhal et al., 1998), the research of using chemicals as a co-injected fluid to hot water or steam has received great attention. Especially in very cost sensitive SAGD operations, a chemical additive may cause promising improvements in steam chamber propagation and heat transfer to mitigate the above mentioned drawbacks.

The chemicals used in this paper were injected initially in SET 1 by a syringe from the top part of the model. In SET 2, the concentration was introduced in predefined fractions at different time sets to evaluate effectiveness at specific times. A high concentration of 10% wt. chemical was used to visualize possible effects properly and was calculated based on the total steam injected. It should be noted, that this concentration is obviously too high for real case scenarios and was selected for visualization and screening purposes only. Table 3.1 shows the studied chemicals. A brief review on the detailed analysis and background experience on these chemicals are presented in the following paragraphs.

Table 3.1: Studied chemicals.

Nr.	Chemical	Concentration
1	Reference	-
2	Biodiesel (Fatty acid methyl ester)	10 %wt.
3	Anionic Surfactant (LTS)	10 %wt.
4	Non-ionic Surfactant 1 (Tween80)	10 %wt.
5	Non-ionic Surfactant 2 (Span80)	10 %wt.
6	Non-ionic Surfactant 3 (Novelfroth 190)	10 %wt.
7	Ionic Liquid [BMMIM BF_4]	10 %wt.
8	Solvent (Heptane (C_7H_{16})	10 %wt.
9	Nanoparticle (Silicon Oxide (SiO_2))	10 %wt.

LTS: Linear Toluene Sulfonate

The combination of steam-solvent injection has been proposed and patented by Nasr et al. (2003). The concept relies on the additional viscosity reduction by the evaporated hydrocarbon additive. The diffusion of the solvent (in this case hexane) exhibited an increase in the oil drainage rate of three times. A comprehensive investigation of solvent-aided SAGD (SA-SAGD) pore scale mechanisms was done by Mohammadzadeh and Chatzis (2010). An interesting observation was made in the convective mass transfer of the SA-SAGD process, where a near-perfect vertical interface was noticed between the liquid solvent and bitumen due to the extensive miscibility of the displacing phase (steam and vaporized solvent). These conclusions are compared in the present paper with the flow of steam with heptane in a Hele-Shaw cell. However, most of the research areas are focused on the co-injection of hydrocarbon solvents, which are relatively cost-effective. Dimethyl ether (DME), as a water-soluble solvent, was recently suggested as an alternative to hydrocarbon solvent. Promising simulation results presented by Sheng et al. (2017b) showed the advantages of DME-SAGD operations, which included a higher chamber-edge temperature, high retrieval of the DME (as it is soluble in water and oil), and a 35% reduction of steam-oil-ratio (SOR). DME is not considered in this paper as the flow behavior is believed to be comparable to heptane.

The application of heat in the reservoir induces already a natural IFT reduction due to the decrease of the cohesive forces of the water/steam. The goal of injecting surfactant as a steam additive is to further reduce the IFT between steam/condensate and heavy oil. A suitable surfactant should be thermally stable to resist decomposition at high temperature environments. Hence, screening tests are mandatory to characterize a chemical's capability at elevated temperatures. Three different kinds of surfactants were examined in potential enhancement of emulsification (micelle flooding) and other typical flow performances. A Biodiesel was suggested and investigated as a steam additive due to its high temperature tolerance showing promising results in recent publications by Babadagli et al. (2010), Babadagli and Ozum (2010), Bruns and Babadagli (2017), and Naderi et al. (2015). The positive effect of Biodiesel was attributed to the hydrophilic methyl ether (COOCH3) group and the hydrophobic hydrocarbon chain with a carboxyl group, which is also a natural surfactant in crude oil. After a heating period of a solution of Biodiesel, the condensate exhibited a creamy/turbid color, which could be referred to as a separating dilute solution phase from the original solution. The precipitation of these aggregates at a specific temperature is also known as the cloud point, which is important for nonionic surfactants because of the decrease in solubility with increase in temperature. Recovery improvement was observed in sandpack experiments conducted by Babadagli and Ozum (2010), Bruns and Babadagli (2017), and Naderi et al. (2015).

The anionic surfactant is a linear toluene sulfonate (LTS) designed for high temperature operations. A comprehensive explanation on its performance, characterization, and applications is given in Barnes et al. (2010) and Buijse et al. (2010). The hydrophilic sulfonate group is negatively charged, which means the LTS characterizes an anionic surfactant. Thermal stabilities of different sulfonates and a nonionic surfactant (alkylphenoxypolyethanol) were already investigated by Handy et al. (1982) with the conclusion of comparable high stabilities for petroleum sulfonates based on the half-life of the components.

As mentioned, anionic surfactants carry a negative charge in the hydrophilic group whereas the non-ionic surfactants have zero net charge. Three different non-ionic surfactants were tested with the presented methodology of Set1. The fatty acid esters of sorbitan with a triester, sorbitan trioleate (Span80), with their ethoxylated products, polyoxyethylene sorbitan tristearate (Tween80), as well as alcohol ethoxylates (Novelfroth190) were considered in this study.

Fluid-solid or fluid-fluid interactions induce potential oil trapping by steam displacement processes as stated and visualized by Mohammadzadeh and Chatzis (2010), where it was shown that the grains tend to be oil wet since an oil film was left behind the propagation steam interface. The wettability of a rock surface and its alteration is a widely discussed and yet not fully clarified parameter, especially in EOR research. Atomic force microscopy (AFM) measurements conducted by Hogshead et al. (2011) of the forces acting between bitumen and silica concluded a reduction of the adhesion force leading to an enhanced separation of the bitumen. An ionic liquid (1-Butyl-2,3-dimethylimidazolium tetrafluoroborate [BMMIM BF_4]), which consists of organic cations associated with anions, was confirmed to be a thermally stable chemical and good wettability alteration agent by Wei and Babadagli (2017). Therefore, the ionic liquid is believed to be a promising chemical additive in dynamic displacement techniques because of its efficiency in rock wettability and/or electrostatic interactions of fluid and solid.

Nanofluids, which are a special prepared fluid with nanoparticles in colloidal suspension, have been tested as an EOR additive to alter surface and interfacial properties (Hendraningrat et al., 2013). Sun et al. (2017b) presented a review paper evaluating the effects of nanofluids on disjoining pressure, pore channel plugging, viscosity increase of injection fluids, IFT reduction, wettability alteration and prevention of asphaltene precipitation. Silicon oxide (SiO_2) was suggested as representative nanoparticle because of its potential in reducing IFT at high temperatures due to its high specific surface area (Alomair et al., 2014) and relatively lower cost for heavy-oil applications (Wei and Babadagli, 2016).

3.4 Results and Discussion

In the following sub-sections, the results of the two conducted experimental sets of (1) top injection without vacuum insulation (lower temperature environment) and (2) side injection with vacuum insulation (higher temperature environment) are presented and discussed for each chemical additive described above. The detailed images of both sets for the base (steam only) case are given in Figures B.1 and B.2 of the Appendix (B) for comparison.

Base Case

Figure 3.2 shows the first minutes of the experiments. In the left picture, steam was injected with a constant rate from the top-center injection port to the bottom-center production port. The right picture depicts the displacement of steam from the side injection port to the bottom with a controlled pressure depletion. When the steam invades into the heavy oil saturated clearance, it transfers the heat into the oil phase and condensates. The displacing water condensate leaves an oil film behind the moving interface. The instability of this displacement (viscous fingering) is due to the high mobility difference of oil and water/vapor. The preferred attraction of the used plexiglass is not known; however, since the oil film is left behind and it is initially saturated and aged with heavy-crude oil, it is assumed to have an oil-wet tendency. The thickness of the film is controlled by the influencing forces of viscosity relative to the surface tension Homsy (1987) and Kong et al. (1992). When injecting from the top with a constant rate (left image, lower temperature experiment), a single dominate finger following the gradient occurs and shields the other fingers from further growth. The right image (higher temperature experiment), however, illustrates a wider spreading of thin fingers. It is believed that the dominant growth of one finger is related to the dominant viscous forces relative to the interfacial tension.

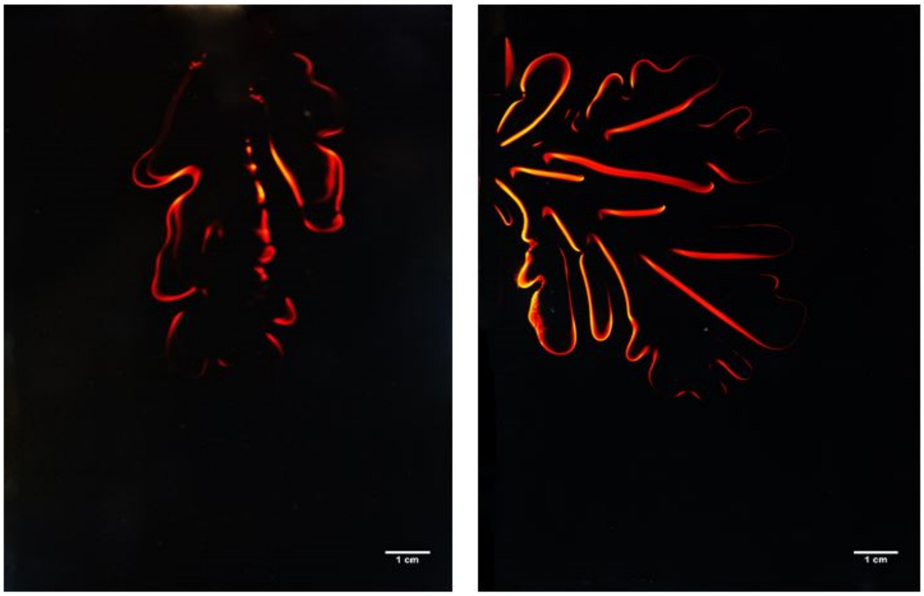


Figure 3.2: Early stage of the Hele Shaw experiment. Condensate displaces the heavy oil with a Laplacian growth pattern. Left: Injection from the top with heat loss. Right: Injection from the side without heat losses.

Figure 3.3 visualizes the further growth of the steam/condensate fingers at the time steps 90 and 240 min (end of experiment). Kong et al. (1992) observed in their visualization study that the steam would follow the path of the water/condensate in the initial stage and a rapid vapor influx would occur. Similar effects were observed during the first set of the Hele-Shaw experiment (Figure 3.3b; white circle area). The temperature profile was visualized with an infrared camera and reached a value of 90°C (+/- 5) at the top injection port (Figure B.3). Based on this we can assume that the condensate moves toward the bottom along with the gradient and is followed by a vapor bubble, which is represented by the clear light breakthrough. As mentioned, the heat is transferred into the oil phase and a phase transition takes place. The flow, however, will only be in the downward direction in a liquid state because of the density difference and acting gravity force. This can be further observed in Figure 3.3c where the oil is displaced by the steam in the upper part. Once a single finger reached the producer, it thinned down until it lost the connection to the injector due to the pressure decrease. The aim is to stabilize the flow behavior of the steam with a chemical additive as will be discussed in the following section.

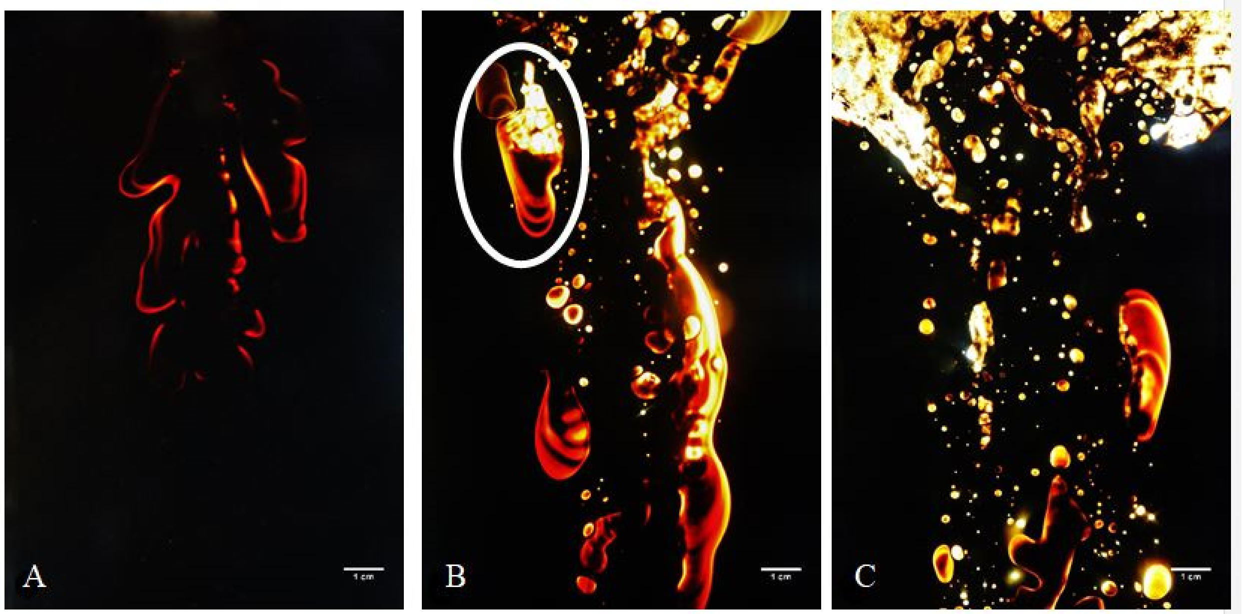


Figure 3.3: Timeframe of the base case experiment SET 1. 3a: Initial stage of experiment T = 5 min; 3b: T = 90 min; 3c: T = 240 min

Figure 3.4 depicts the images of the second set of experiments taken at 30 and 60 min. Steam was injected from the side with the prevention of heat loss this time due to applied vacuum. Thus, temperature inside the steam chamber should be higher than 100°C with deviations at specific positions (edge of steam chamber) as saturated steam was injected with a temperature of 200°C. It can be noted that the steam chamber growth was smoothly and continuously compared to the first set (Figure 3.3) indicating more gravity- stable displacement. Similar to the other set given in Fig. 3.3, initially, steam followed the instable condensate fingers (Figures 3.4a and 3.4b). Then, the stable interface between the heavy oil and steam propagated towards the top of the Hele-Shaw cell developing a chamber as a reminiscent of the SAGD process. The lower fingers broke up after establishing a connection to the production port due to the pressure drop. This experiment verified the importance of the phase of the injected water/steam controlled by temperature (and heat losses) on the displacement stability and efficiency, eventually the resulting steam-to-oil ratio.

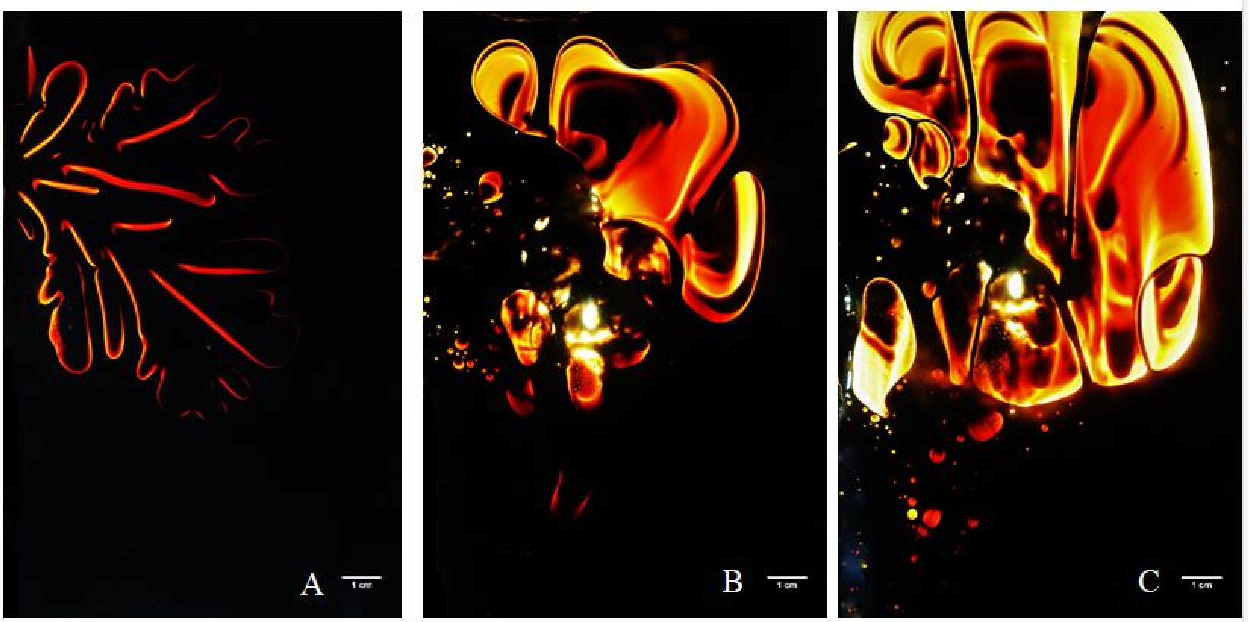


Figure 3.4: Timeframe of the base case experiment SET 2. 4a: Initial stage of experiment T = 5 min; 4b: T = 30 min; 4c: T = 60 min.

Differences in the sizes of the inner phase of the emulsions formed are observed as illustrated in Figure 3.5. Circle A highlights the microemulsions of water in the oil film sticking to the surface of the plexiglass while the steam phase is flowing into the system. Furthermore, most of the oil is produced with the downward flow of condensate emulsions (Figure 3.5, circle B) towards the production port (Figure 3.4c). However, residual oil interpreted by the orange/yellow color was still left behind the advancing steam chamber growth.

Biodiesel

Figure 3.6 illustrates the displacement experiments with Biodiesel as a chemical additive. As mentioned, the chemical was introduced before steam entered the cell. A dominant single finger moved from the injection port downwards to the producer (Figure 3.6a). Furthermore, this finger was thinner compared to the tip-split fingers in the beginning of pure steam injection. The strong light reflection indicates a clear surface that was left behind the displacing fluid. The influencing factors in the dominance of a single finger need further investigations.

A thin finger with a smaller interface identifies a higher IFT than with a bigger interface in the

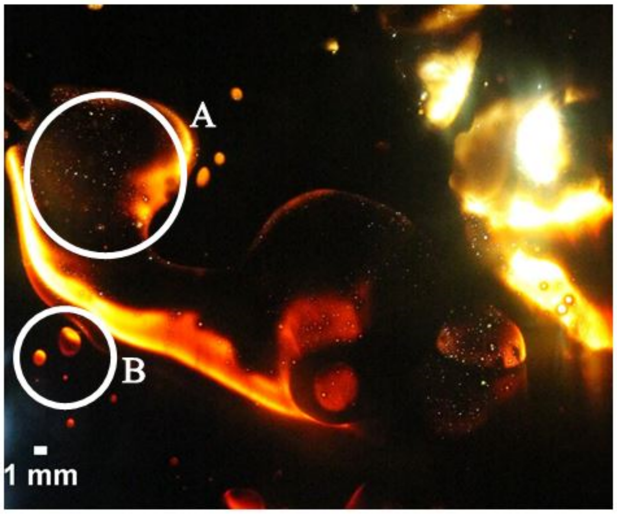


Figure 3.5: Differences in emulsification of water/condensate in oil. Picture taken close to injection port at T = 42 min.

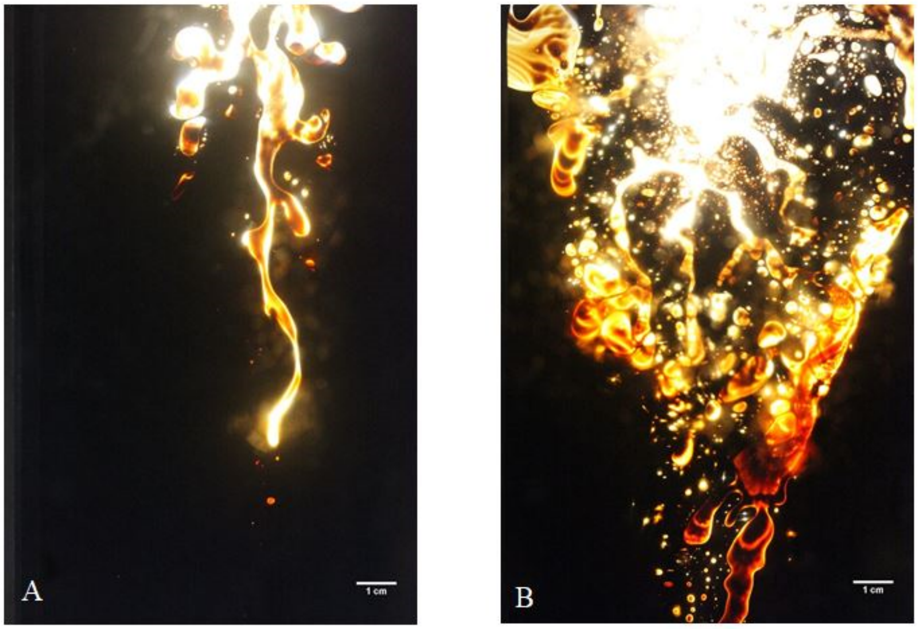


Figure 3.6: Hele Shaw experiment SET 1 with Biodiesel. Steam injection from the top part of the cell. 6a: Initial stage of experiment T = 5 min; 6b: T = 240 min.

base case experiment. Figure 3.6b shows the end of the experiment with Biodiesel as an additive. In contrast to the base case experiments (Figures 3.3 and 3.4), the surface around the injection port is cleared from oil. A possible explanation for this could be the high solubility of the chemical in bitumen where the compositional change might have caused a change in surface tension. Babadagli and Ozum (2010) mentioned that solubility of the Biodiesel cause limitation in efficiency of acting as a surfactant additive and the issue could be the explanations for the case in our images (an immediate dissolution of the chemical into the bitumen/heavy oil close to the wellbore area). Based on these observations, an initial injection of Biodiesel may not be recommended if it is a more viscous-driven process. Figure 3.7 visualizes the steam chamber growth including Biodiesel neglecting heat losses. Similar effects of sweeping the near region of the injection of can be observed

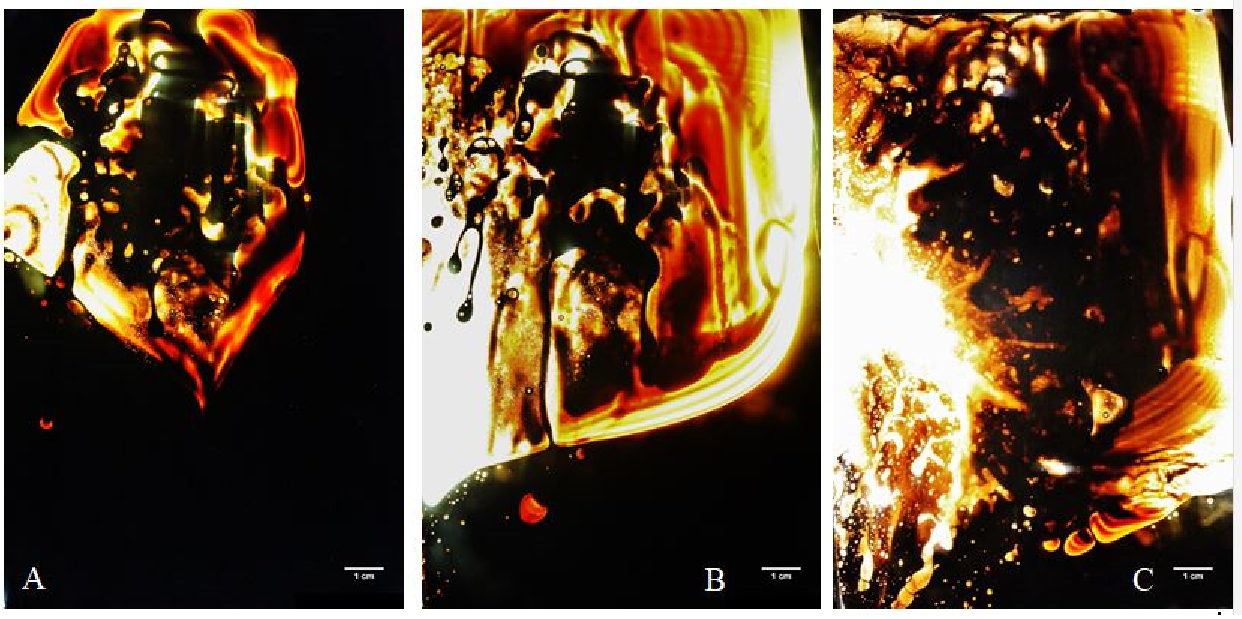


Figure 3.7: Timeframe of the Biodiesel experiment SET 2. Steam + chemical additive injected from the side. 7a: Initial stage of experiment T = 30 min; 7b: T = 120 min; 7c: T = 240 min.

with a constant injection rate of the chemical. Nevertheless, Biodiesel could be a potential stabilizer in the startup phase of a steam injection process if it is gravity dominated flow. By comparing the pictures taken at the same time in Figure 3.7a with Figure 3.4b, the steam chamber did not follow condensate paths with the co-injection of the Biodiesel. This efficiency of enhancing flow performances in the initial stage is also proven with the coreflood experiments conducted by Bruns and Babadagli (2017), where extraordinary inclination of production was measured at the beginning of the experiment.

Heptane

The miscibility of the solvent in oil causes additional viscosity variations to the temperature effects by steam. A typical visualization of viscous fingering by miscible displacement can be noticed in Figure 3.8a showing the initial stage of the Hele-Shaw experiment SET 1, where the pure solvent diffuses into the oil over time. The difference between injection of a miscible fluid to an immiscible one is the absence of a clear interface due to the neutral IFT as the tip of the fingers slowly diminished over the length of the cell. Shortly after the solvent was introduced into the cell, the steam followed with a constant injection rate. Figure 3.8b shows the next adjacent stage of the experiment after 30 min of steam injection. Identical to the base case, a single finger defines the connection between the injection port and the production port due to high mobility differences. Figure 3.8c represents the final stage of the solvent injection experiment. A clear interface of steam, condensate and heavy oil can be distinguished from the base case (Figure 3.3c). An improvement of reducing the viscous drag force was achieved by the dissolution of the solvent into the oil phase. Thus, the viscosity reduction of the oil is a result of the asphaltene precipitation and deposition. The asphaltene deposition is notable in Figure 3.8c (circle A) as similar to observations by Das and Butler (1998).

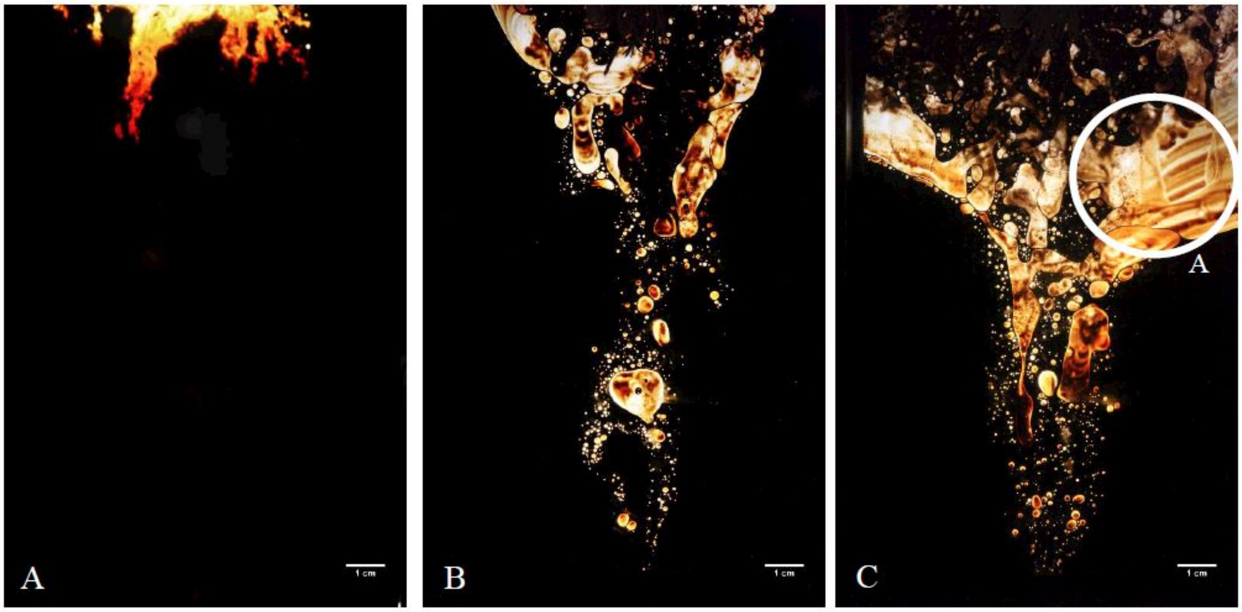


Figure 3.8: Timeframe of the solvent experiment SET 1. Steam + chemical additive (Heptane) was injected from the top. 8a: Initial stage of experiment T = 0 - 5 min; 8b: T = 90 min; 8c: T = 240 min.

The space of the channel was occupied with dispersions of liquid droplets (Figure 3.8b and 3.8c). The quantity of these emulsions is in several orders of magnitude higher compared with the base case. Water-in-oil emulsions should flocculate or coalesce because of the small electrostatic and steric forces considering that no stability agent (i.e., surfactant) was injected with the solvent. Hence, the assumption is a development of emulsion stabilization by the precipitated asphaltenes. Figure 3.9 depicts the diffusion of heptane into the oil film left behind the propagating steam interface.

The pictures were taken in a timeframe of three min where a small amount of solvent concentration of 0.6%wt. was injected into the cell. The residual oil was removed by the dissolution of the heptane within the steam chamber under high temperature condition.

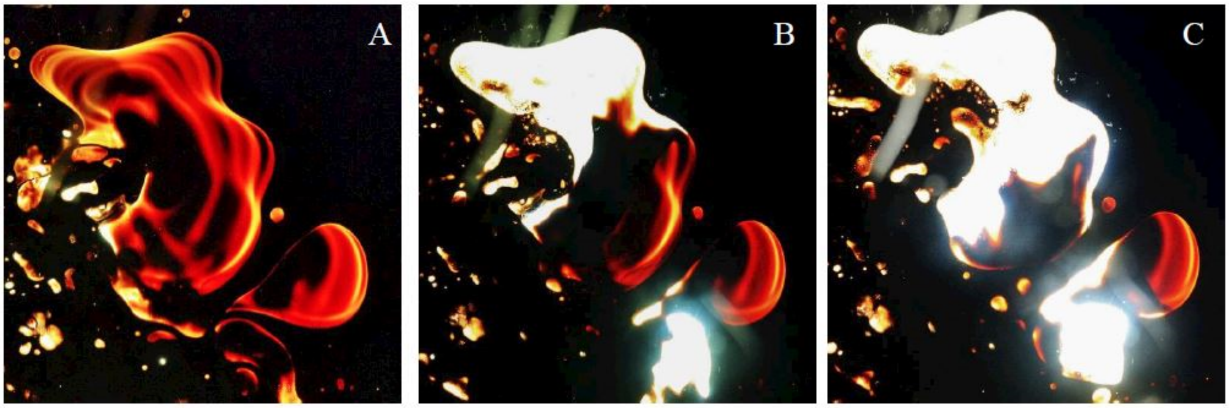


Figure 3.9: Diffusion of the solvent (heptane) inside steam chamber over the time.

Ionic Liquid BMMIM BF_4

base case scenario, a high quantity of condensate was never attached to the surface during any stages of the experiment and the expanding steam chamber did not displace the oil phase completely. The experiment including the ionic liquid, however, exhibited extraordinary generation of condensate/oil clusters with liquid bubbles adhering to the plexiglass surface (Figure 3.10b, red circles). In addition, the residual oil drained downwards as pointed out in Figure 3.10 by the moving interface from the top. After the experiment was repeated and similar effects were observed, it can be concluded that the mechanics of the ionic liquid allowed a decrease of work needed for detaching the oil from the

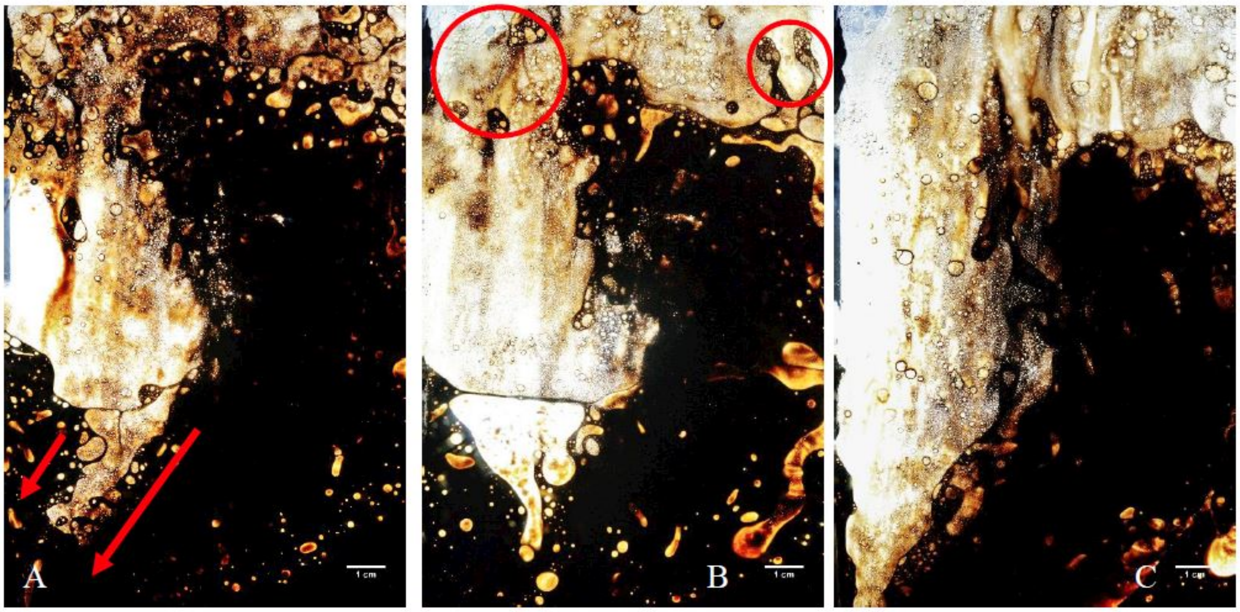


Figure 3.10: Timeframe of the ionic liquid experiment SET 2. Steam + chemical additive were injected from the side. 10a: T = 120 min; 10b: T = 150 min; 10c: T = 180 min.

surface of the plexiglass. With the expectation that an attractive force constructs a liquid oil film after mechanical and thermal energy was applied, the ionic liquid could have treated the surface to enhance the oil + condensate drainage. These assumed mechanisms of enhancing flow performances by adding an ionic liquid were not observed during the first set of experiments (Figure 3.11).

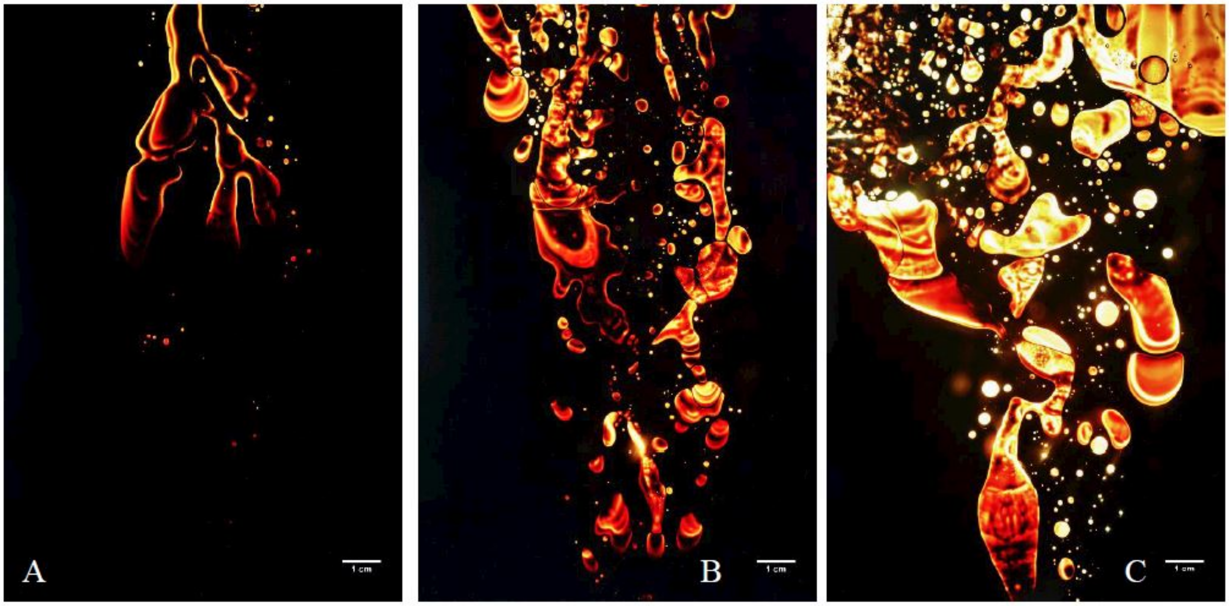


Figure 3.11: Timeframe of ionic liquid experiment SET 1. Steam + chemical additive were injected from the top. 11a: Initial stage of experiment T = 0-5 min; 11b: T = 120 min; 11c: T = 240 min.

The physics of the displacement was comparable with the base case scenario. A possible error could be the straight mass transport of the chemical to the production port due to viscous fingering and the initial injection procedure.

Anionic Surfactant - LTS

Spreading nature of displacing fingers is a function of surface tension variations, as already explained in the base case experiment. The first set of experiments was characterized by a flow path in the center of the cell. Figure 3.12 shows the selected stages of the experiment injecting a linear toluene sulfonate (LTS) with steam from the top of the Hele-Shaw cell with a constant injection rate. The initial stage of this experiment differed in the condensate fingering where no clear interface of an advancing front occurred. An explanation for this is the injection of the chemical concentration resulting in a flow path for the following steam. However, attention can be paid to the stages of Figure 3.12b and Figure 3.12c. Figure 3.12b depicts the flow of the displacing steam where a spreading can be observed. This spreading phenomenon is a function of surface tension (Homsy, 1987). Considering the surfactant acted at the surface and lowered the interfacial tension, the

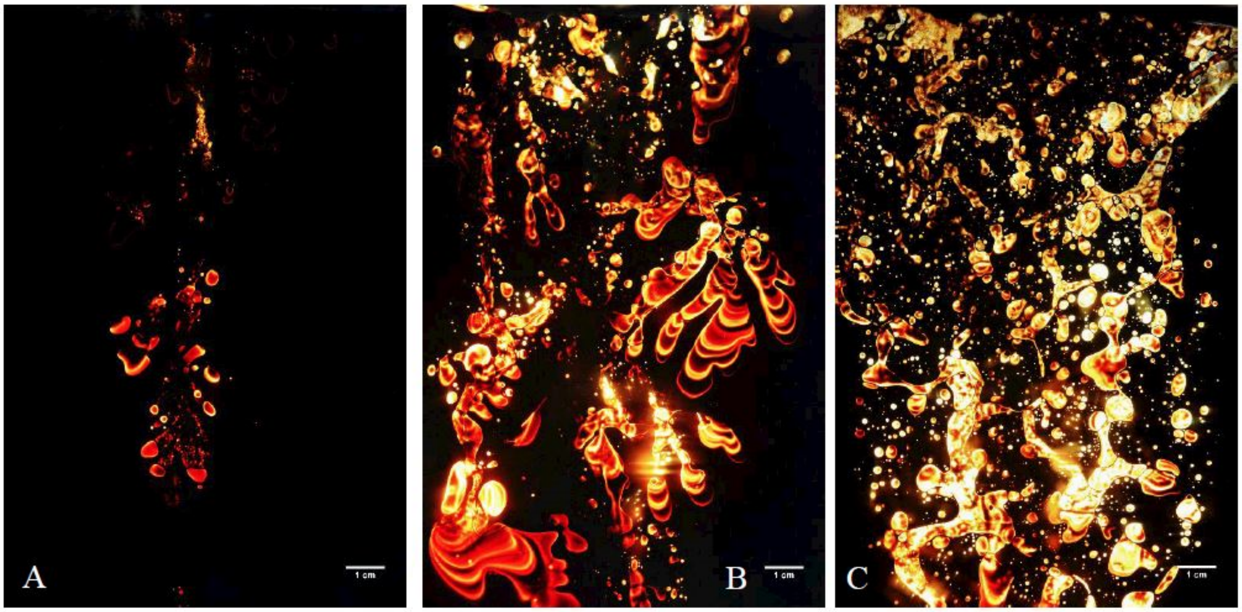


Figure 3.12: Timeframe of the anionic surfactant experiment SET 1. Steam + chemical additive were injected from the top. 12a: Initial stage of experiment T = 0-5 min; 12b: T = 120 min; 12c: T = 240 min.

fronts of the finger became unstable and, thus, tip splitting of the finger commenced. As a result, a wider area of the cell was occupied by the displacing fluid, which is displayed in Figure 3.12c. The performance of this surfactant in a steam chamber is shown in Figure 3.13. The beginning of the experiment (Figure 3.13a) behaved analogously to the base case scenario. Steam accumulated

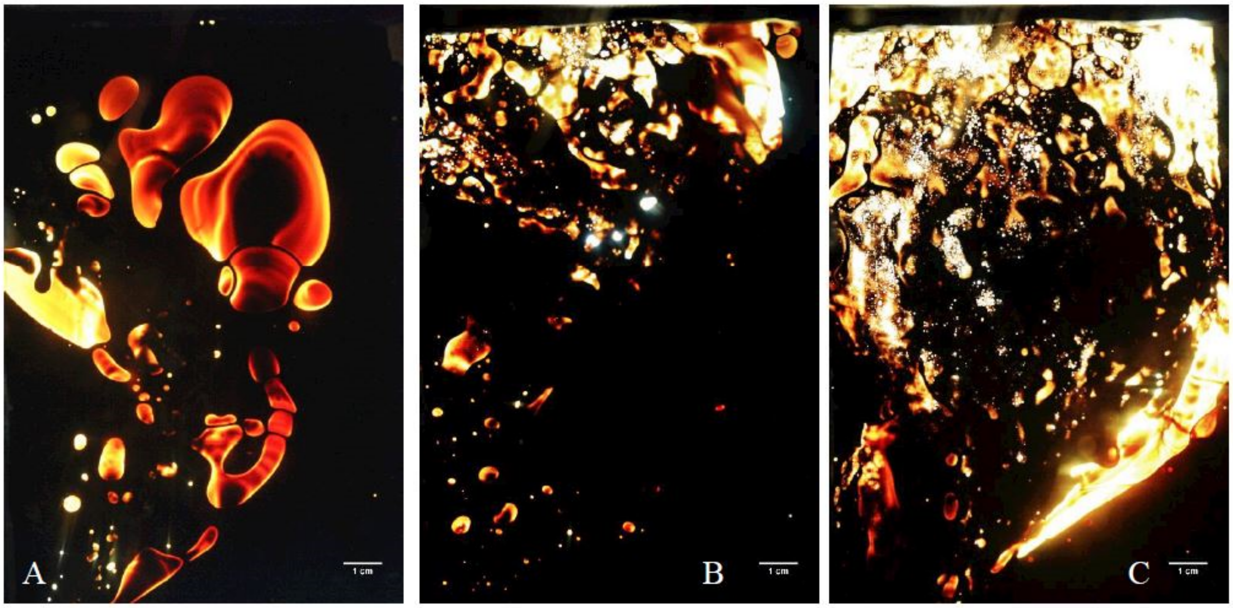


Figure 3.13: Timeframe of the anionic surfactant experiment SET 2. Steam + chemical additive were injected from the side. 13a: T = 30 min; 13b: T = 120 min; 13c: T = 180 min.

at the top and condensate drained towards the production port. Water droplets engulfed into the oil phase identically to the effects examined with the ionic liquid.

Nanoparticle - Silicon Oxide

Figure 3.14 shows the nanoparticle experiment SET1. In the early stage, emulsions were flowing in a downward direction where no typical Laplacian growth pattern of the condensate fingering could be observed, as opposed to the anionic surfactant experiment, where wider occupation of the steam can be concluded. Adsorption of the solid particles, such as a nanoparticle, at the liquid-liquid interface is the key mechanism of the Pickering emulsion. The surfaces of the solid particles are partially wetted and this results in very stable emulsion depending on the hydrophobicity of the particle. A higher quantity of condensate emulsions was noticed, which can be a result of Pickering emulsions. These types of emulsions can also lead to an enhanced conduction of heat transfer. Analysis of temperature distributions within the Hele-Shaw cell could lead to clarification of these mechanisms. Further improvements cannot be classified. The co-injection of the nanoparticle with the steam in SET 2 did not give conclusive improvement in flow mechanisms.

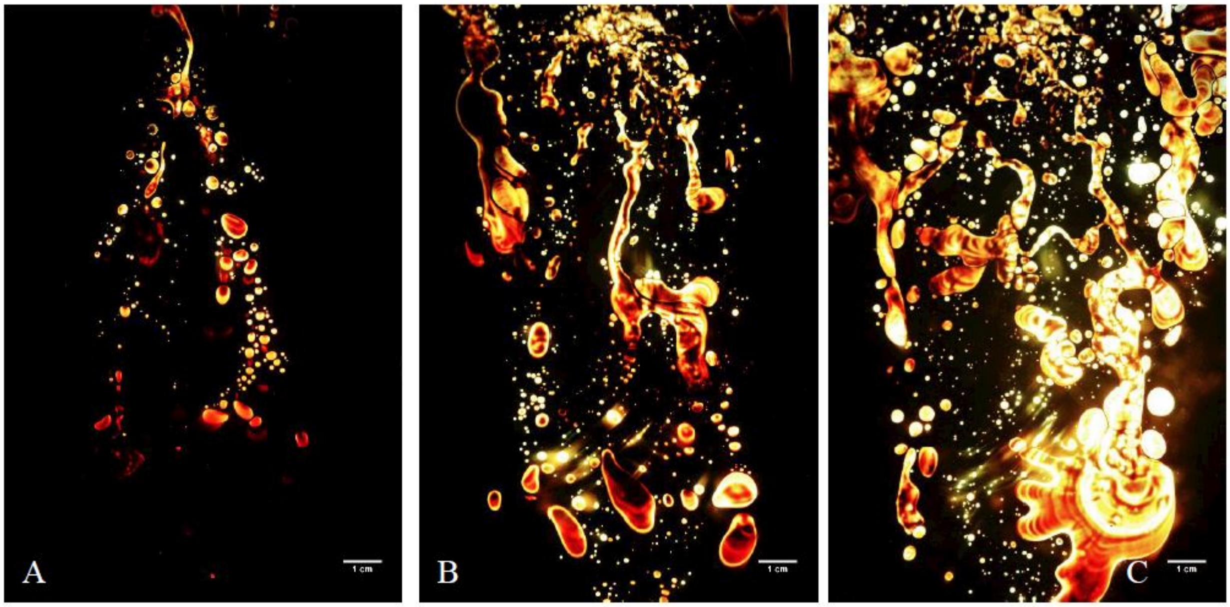
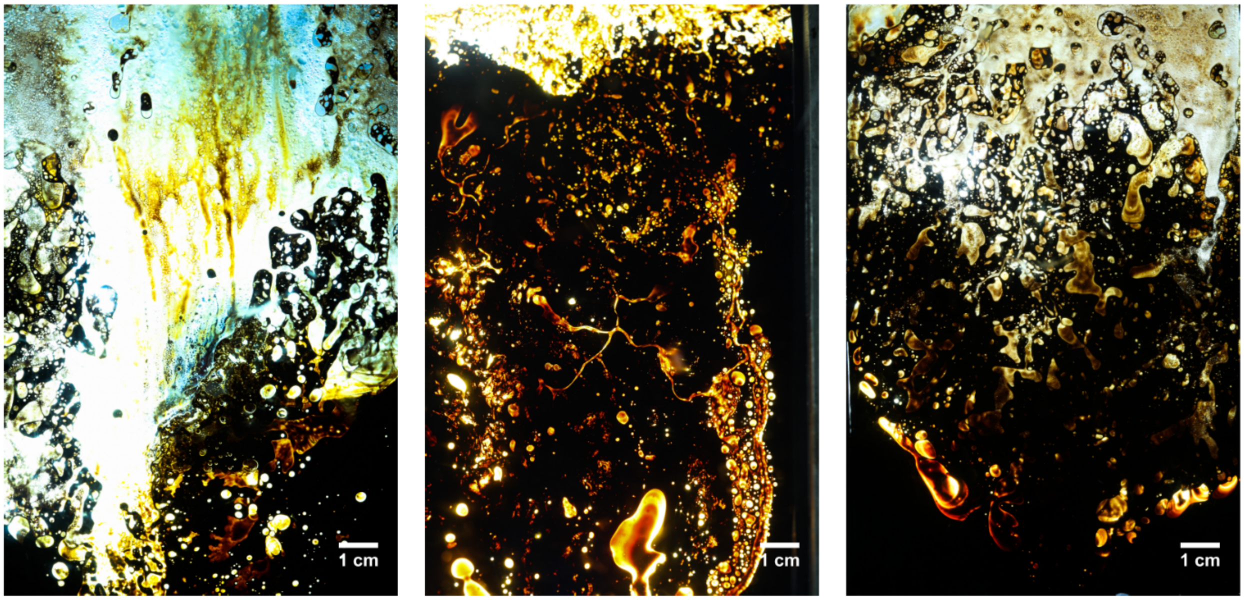


Figure 3.14: Timeframe of the nanoparticle experiment SET 1. Steam + chemical additive were injected from the top. 14a: T = Start up; 14b: T = 120 min; 14c: T = 240 min.

Non-Ionic Surfactants - Tween80, Span80, Novelfroth190

Tween80, Span80 and Novelfroth190 were selected as representatives for non-ionic surfactants. All the chemicals show different characteristics in molecular structure. Tween surfactants (here polyoxyethylene sorbitan monooleate) is produced by ethoxylation of Span (here sorbitan monooleate) with ethylene oxide in reaction with the hydroxyl groups. Therefore, the Tween surfactants with a high hydrophilic-lipophilic balance (HLB) value become more water soluble compared to the Span surfactants with a low HLB value. Based on this and reported by Apenten and Zhu (1996), Span surfactants tend to generate water in oil (W/O) emulsions due to their low HLP whereas Tween surfactants promote oil in water (O/W) emulsions with their high HLB value at the interface. Similarly, a high HLB value of 11.0 was measured by Gupta and Zeidani (2013b) for the alcohol ethoxylate, Novelfroth190, which would imply a preference of O/W emulsification at the oil and water interface. Figure 3.15 shows pictures taken at the near end (T = 200 min) of the experiments where Tween80, Span80 and Novelfroth190 were initially injected into the cell.

Tween80 and Novelfroth190 exhibited similar behavior to the ionic liquid. Condensate attached in the top region of the Hele-Shaw cell on the plexiglass which was also observed injecting an ionic liquid. For the specific mechanisms to be identified for these results, further tests and quantification of parameters are required. In this experiment, the plexiglass represents rock surface which includes uncertainties for instance surface charge and wettability. Comparing the visualization of the Tween80 and Novelfroth190 with the Span80, a larger swept area can be noticed. Furthermore, a condensate finger moved downwards with a high quantity of w/o emulsions. Based on these results from this methodology, the mechanics of using non-ionic surfactants are dependent on HLB values and emulsification capabilities under high temperature conditions. Since the surfactants have a zero net charge, it was assumed that the surfactant only



(a) Tween80 (b) Span80 (c) Novelfroth190

Figure 3.15: Non-ionic surfactants Tween80, Span80 and Novelfroth190 experiment SET1 at late stages. Steam + chemical additive were injected from the top. 15a: Tween80; 14b: Span80; 14c: Novelfroth190.

act on the interface and do not adsorb on the plexiglass surface.

3.5 Conclusions

Different chemical additives to steam were evaluated to clarify their contribution to potential recovery improvements and the physics behind the process. Two types of experiments were conducted with a Hele-Shaw cell to analyze the effects of specific conditions including viscous or gravity dominated displacement, distinct surface alterations, heat transfer, and chemical type. The following conclusions can be withdrawn from this study:

1. Biodiesel exhibited diffusion into the oil phase close to the injection port where the residual oil film was removed. Instabilities in the displacement of steam were still observed in both experiments; however, an initial injection could lead to an enhanced steam chamber growth in SAGD operation as the expansion of the chamber was not a dependent on the condensate paths. A determination of injection time for this type of surfactant is crucial.
2. Solvent injection led to an improvement in oil drainage due to the precipitation of asphaltene and the following viscosity reduction. Different injection strategies were proposed throughout the years, but high efficiency inside the steam chamber was noticed when the solvent/steam solution displaced the residual oil. Therefore, the introduction of the solvent into the reservoir is recommended in a later stage of a steam injection operation.
3. Alteration of solid-liquid interactions was monitored based on the flow behavior of condensate/oil on the plexiglass during the injection of an ionic liquid. Condensate droplets instead of oil film adhered to the plexiglass surface, which was never the case in this quantity for other tested chemicals. It was concluded and supported by the literature that the ionic liquid changes wettability preferences of the solid under high temperature conditions. Oil film drainage is followed along the solid surface.
4. A wider occupation of the cell was recorded by injecting an anionic surfactant, a linear toluene sulfonate. Assumptions of IFT alterations were made whereby a higher tip-splitting frequency of the displacing fingers was followed. Sulfonates are supposed to be more temperature resistant and, hence, are applicable for steam flood applications. Based on this research, the surfactant should be injected in a later stage where a steam chamber is already established to minimize time of high temperature exposure and to obtain the required improvements along the steam chamber edge.
5. Similar behavior of tip-splitting was determined by introducing a nanoparticle, silicon oxide, and the accompanying mechanism of reducing IFT between steam/condensate and oil. It is

believed that the nanoparticle can improve heavy oil drainage by creating emulsification due to Pickering emulsions. Additionally, investigation of improving heat transfer is required and considered for further research based on the thermal conductivity while a nanoparticle acts at the interface.

6. Non-ionic surfactants were tested in the Set 1 methodology and showed different emulsion capabilities. The Span80, a sorbitan monooleate, a high quantity of water in oil (W/O) emulsions was recorded which can be explained by the low HLB value. The ethoxylated derivate, Tween 80, as well as the alcohol ethoxylate, Novelfroth 190, with high HLB values showed improvement of displacement efficiency by removing the residual oil film from the plexiglass surface. Based on this, a higher HLB value may be preferable in steam applications.

Chapter 4

General Conclusions, Contributions and Future Work

Characteristics of novel chemical additives for thermal recovery processes were examined by conducting artificial sandpack and Hele-Shaw experiments with heavy oil. The chemical database consisted of anionic surfactants (O332, LTS-18), non-ionic surfactants (Tween, Span, Triton, Novelfroth), biodiesel, ionic liquid (BMMIM BF_4), high pH solution ($NaBO_2$), solvents (heptane, DME), and a nanoparticle (SiO_2). Thermal stability was tested on all samples by running thermogravimetric analysis (TGA) tests. The oil recoveries of the chemical co-injection were compared and evaluated with the commercial prices. Contribution to potential recovery improvements and the physics behind this was clarified by visualizing steam/chemical displacement in a Hele-Shaw cell. Summarizing this work, the following conclusions can be made:

1. Heptane injection led to an improvement in oil drainage due to the precipitation of asphaltene and the following viscosity reduction. Asphaltene precipitation was proven as a supporting mechanism by conducting SARA analysis. Heptane was the most successful chemical to improve SOR by the significant increase the oil recovery. As one of the cheapest chemicals of the products tested in this research, hydrocarbon solvent injection can be recommended for future developments.
2. Biodiesel, a fatty acid methyl ester, could increase oil recovery yielding the third lowest SOR ratio. In the visualization study, biodiesel exhibited diffusion into the oil phase close to the injection port where the residual oil film was removed. Biodiesel is a promising chemical since it was very efficient in SOR and the lowest commercial price. Therefore, further research is suggested to identify the contributing mechanisms of biodiesel as the diffusivity was not considered in this study.
3. From the anionic surfactants tested, the chemical agent LTS-18, a linear toluene sulfonate, is a promising surfactant in the application of steam injection. Wider occupation of the cell was recorded in the Hele-Shaw experiments by injecting the LTS. Assumptions of IFT alterations were made due to a higher tip-splitting frequency. Sulfonates showed mass degradation in

the TGA tests assuming dehydration of the chemical. Based on this research, the surfactant should be injected in a later stage to minimize time of high temperature exposure.

4. Non-ionic surfactants exhibited great thermal stability in the TGA tests. Specifically, the non-ionic surfactants Span80, Tween80 and Novelfroth190 performed well in steam injection processes. The Span80, a sorbitan monooleate, a high quantity of water in oil (W/O) emulsions was observed which can be explained by the low HLB value. Improvement of displacement efficiency by removing the residual oil film in the Hele-Shaw cell were visualized by injecting the ethoxylated derivative, Tween 80, as well as the alcohol ethoxylate, Novelfroth 190, with high HLB values. According to this observation, a higher HLB value may be preferable in steam applications.
5. Ionic liquid was efficient at the tertiary steam injection stage with a temperature of 150°C as well as with the initial injection into the coreholder. Nevertheless, the ionic liquid used was the most expensive chemical from the product matrix. In the Hele-Shaw experiment, alteration of solid-liquid interactions was monitored based on the flow behavior of condensate/oil on the plexiglass during the injection of an ionic liquid. It was concluded and supported by the literature that the ionic liquid changes wettability preferences of the solid under high temperature conditions.
6. A nanoparticle, SiO_2, was dispersed in the water phase where the injection of this additive ranked as second lowest SOR. However, the purchased nanofluid was the second most expensive chemical measured by the available, commercial prices. Similar behavior of tip-splitting to the LTS was determined between steam/condensate and oil in the visualization study. Pickering emulsions triggered by the nanoparticles are believed to improve heavy oil drainage. Additionally, investigation of improving heat transfer is required for further research based on the thermal conductivity while a nanoparticle acts at the interface.

Future Work

Management of a research project is a function of time, resources and accuracy which always creates limitations in each project. Therefore, these limitations can be solved by developing and conducting further experiments. Based on the conclusions, assumptions and uncertainties in this work, the following steps are suggested for detailed understanding and confident recommendations of field implementations:

Emulsification Study. Emulsions can have a huge impact in flow resistance and phase behavior. When injecting steam into the reservoir, the transferred heat reduces interfacial tension which triggers emulsification of water and oil as primary fluid phases. Specifically, water in oil (W/O) emulsions can be accounted as a drawback in thermal applications due to the viscosity increase of the oil phase. Following this, surfactants are introduced to demulsify W/O emulsions and promote generation of O/W emulsions. To investigate this effect with the amphiphilic molecules, glass tube experiments are recommended with oil and water as two immiscible fluids using surfactants at different temperatures. Non-ionic surfactants exhibited great thermal stability. Nevertheless, it is known that emulsion behavior changes from oil in water O/W to W/O emulsions with increase in salinity (for ionic surfactants) or temperature (for non-ionic surfactants). Further clarification of the sensitivity regarding to the connection of salinity and temperature to the surfactant type is required.

Optimal Concentration. As mentioned in Section 2.3, the experiments in this work were not designed for the analysis of optimal chemical concentration since time and resources were limited. For determination of the concentration for surfactants and other chemicals, IFT measurements at room temperature are recommended to measure maximum decrease in surface tension with increasing concentration. Then, the data can be used to calculate surface excess concentration as well as critical micelle concentration (CMC). Further on, viscosity measurements and quantification of asphaltene precipitation may validate the selection of a specific concentration using solvents.

Compositional Analysis. The results obtained from this study may deviate when a different oil is used. Therefore, it is important to break down the composition of the chemical and the oil to analyze physical and chemical interactions between the components. Based on this, correlations can be developed and normalized so that adaptability and design criteria of the additive can be followed readily by these correlations.

Sensitivity Analysis and other Measurements. As already indicated above, changing parameters, such as pH value (content of divalent ions) or fines content, with the effects on chemical screening need to be validated and quantified. Especially fines, such as clay, can be surface active and stabilize emulsions which causes phase separation problems in the downstream cycle. A chemical can potentially prevent these reactions. Moreover, improvements in heat transfer caused by nanoparticles or even other chemicals should be further investigated particularly at the steam/condensate/oil interface. In general, modified experiments with the designed Hele-Shaw methodology are suggested to ascertain the physics at the steam chamber interface using a chemical. Close images by implementing a microscope into the setup could lead to high impact interpretation of improved flow behavior by chemical additives.

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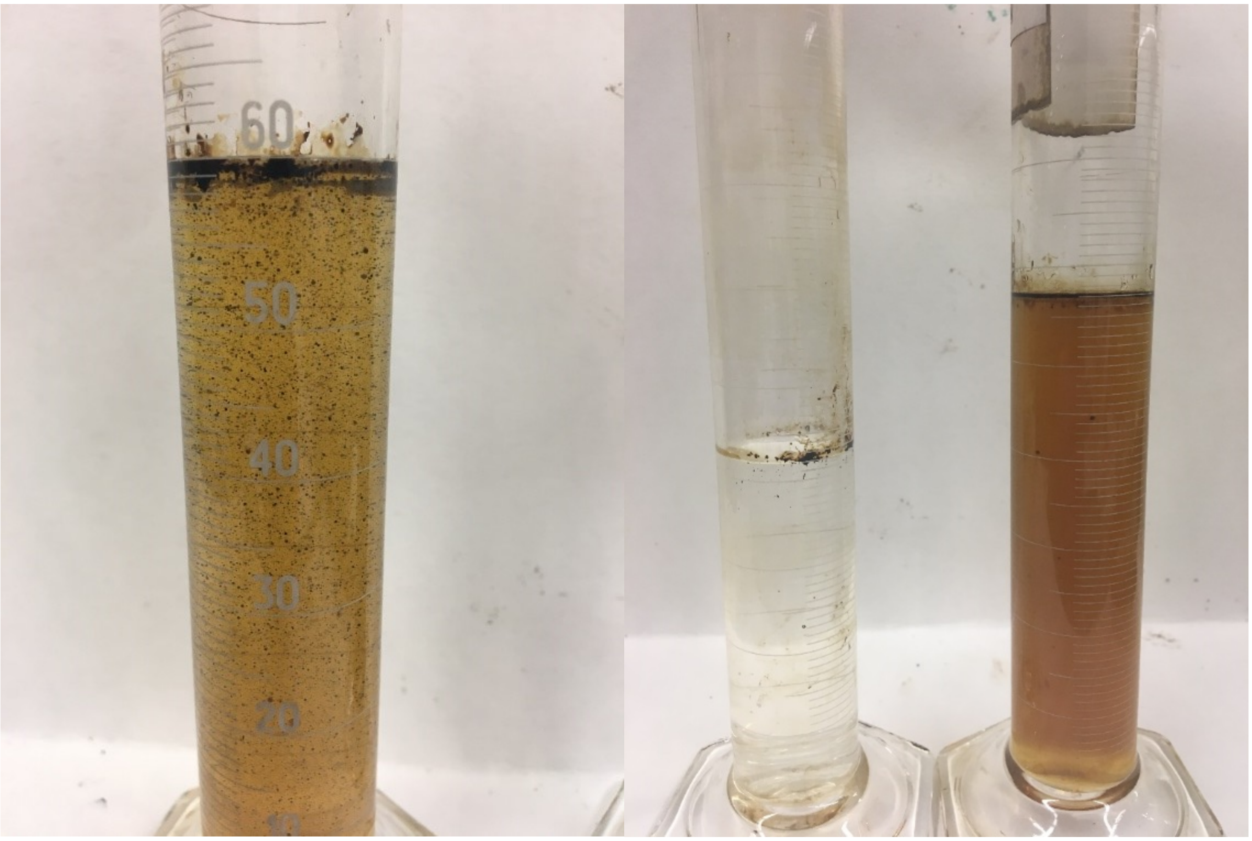
Appendix A

Chapter 2



(a) Triton X-100 **(b)** Tween80

Figure A.1: Separated water phases from the Triton X-100 (left) and Tween80 (right) experiments.

Preliminary High Pressure Tests

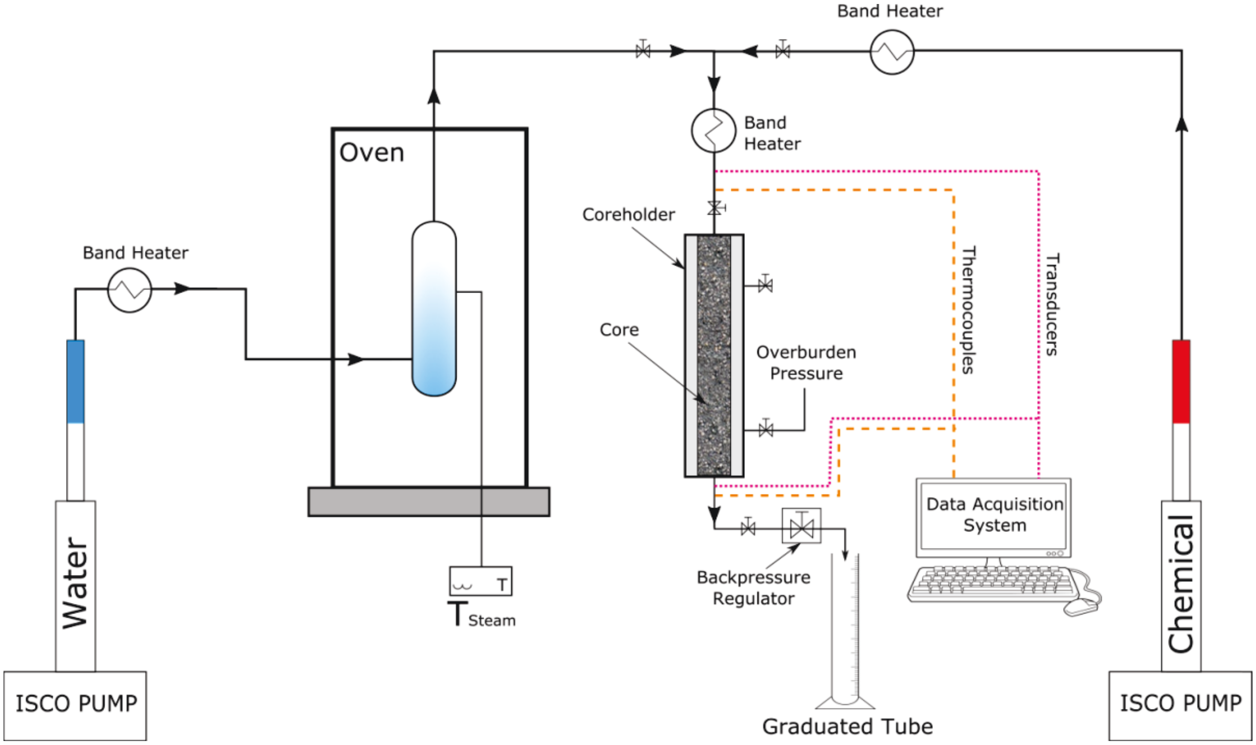


Figure A.2: Schematic of the preliminary high pressure dynamic sandpack experiments.

Reference test. The pressure and temperature profile of the high pressure steam test is shown in Figure A.3. The pressure difference is kept small over the time (10-25 psi). The increase in outlet temperature shows a linear relation. After 540 minutes the slope rapidly changed until a steam temperature (100°C) or steam breakthrough was reached after 600 minutes. Further on, the cumulative oil production is related to the outlet temperature (Figure A.3).

A linear increase in oil production can be monitored with an increasing temperature. Once the steam reached the bottom just before its breakthrough, temperature acceleration started at the outlet (around 540 minutes) and the oil production accelerated proportionally with increasing temperature. With a purely gravity dominated flow of steam through the sandpack, an oil recovery of 44.7% was achieved (red curve in Figure A.4). This control experiment was repeated for reproducibility and a similar trend and ultimate recovery was observed (orange color). The shape of the production curve does not match with the typical recovery curve, where the oil production reaches a plateau as the measurement was stopped after steam breakthrough due to impossibility of quantifying the oil accurately. Hence, the evaluations were made until breakthrough time.

The next phase of experiments included chemical additives. The saturated steam (Temperature

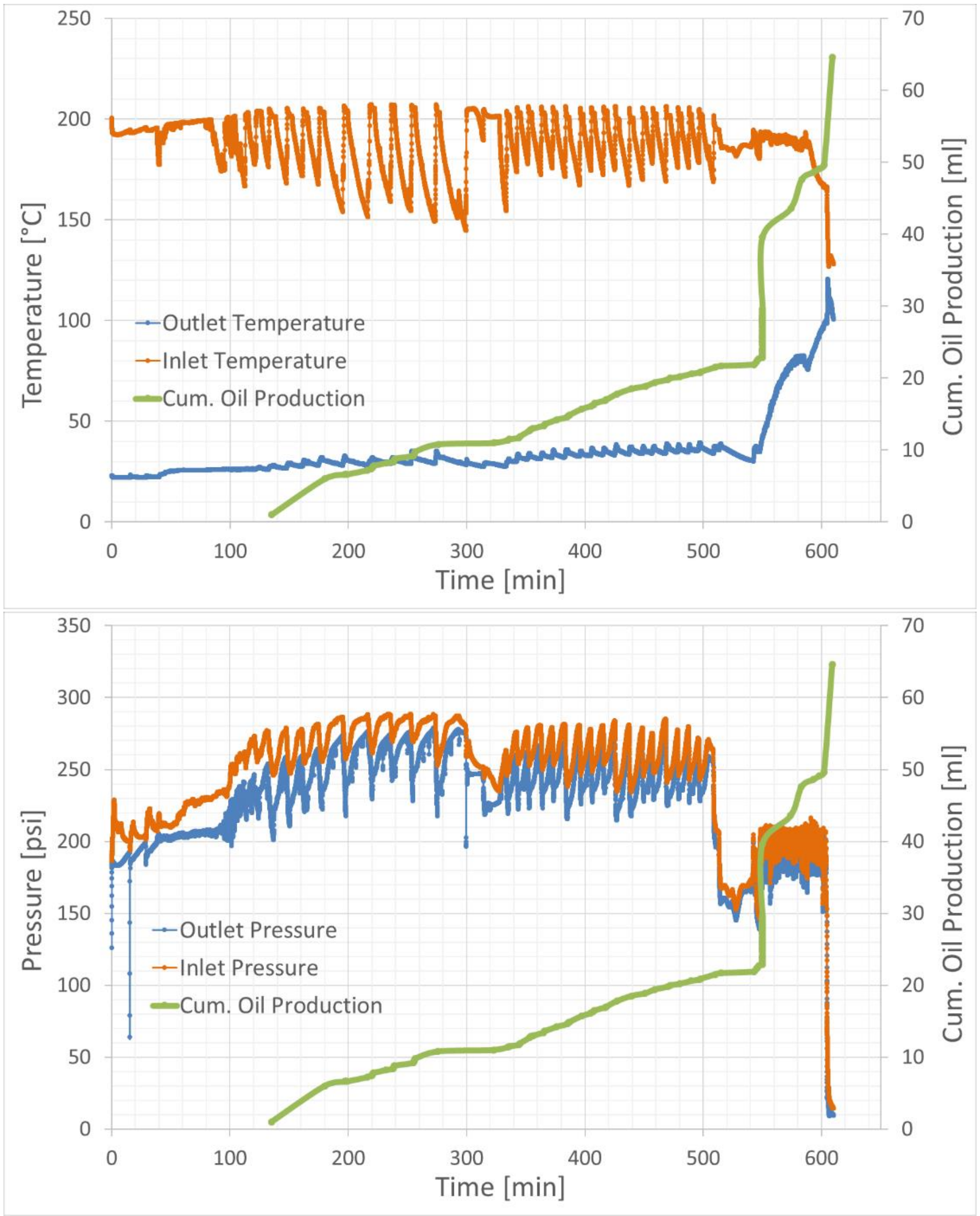


Figure A.3: Temperature (top) and pressure (bottom) profile of the reference test with only steam and oil.

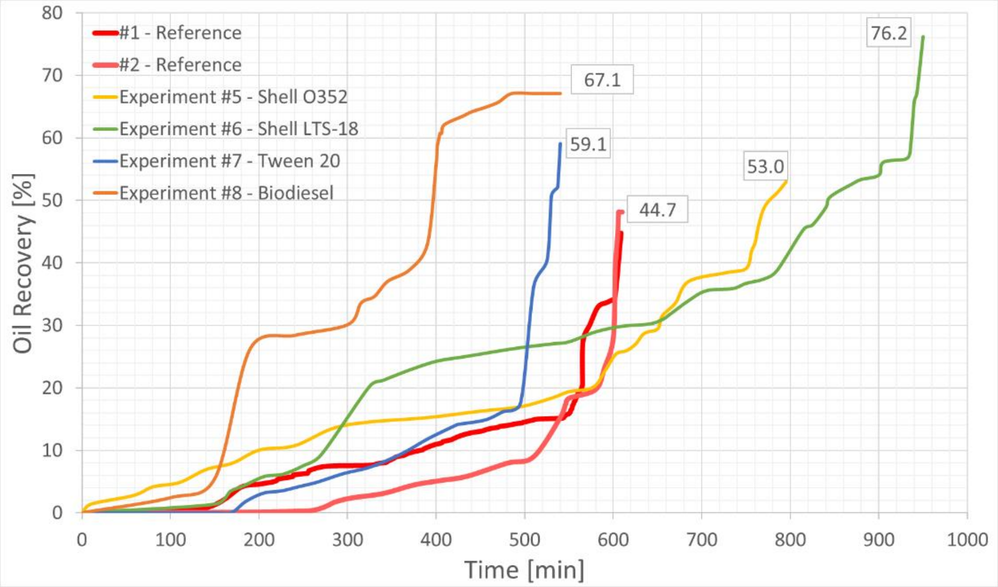
200°C) flowed together into the core with a vaporized chemical solution/water with less quality (Temperature ±150°C) when chemicals were added.

Tertiary injection. The purpose of the tertiary injection was to investigate if hot water injection (60°C) with a chemical compound can enhance the oil recovery after thermal gravity drainage processes. The sandpack was flooded with a high-pressure steam before the injection of the chemicals selected for hot water injection. Three experiments were conducted with the surfactant AAS J11111 (alcohol alkoxy sulfate), AAS J11111 plus sodium chloride (AS-flood), and ionic liquid [BMMIM BF_4]. The maximum temperature of the surfactant AAS J11111 is limited to 60°C, which makes it only suitable for water in the liquid phase. After the steam flood, the system was cooled down to ensure certain properties of the environment for 2 hours before starting the injection of the solution. Hot water injection with a chemical solution does not achieve an enhancement in oil recovery. The water phase with the surfactant was reproduced without any content of oil. ionic liquid, however, was injected in the gaseous phase with a temperature around 150°C and increased the oil recovery by around 20% (Table A.1). The oil recovery was measured by volume which combines higher magnitude of errors (no distinct liquid separation). Further on, the integrated viscous forces (flow rate 5 ml/min) were higher than in the previously presented methodology which also impacted the increment in oil recovery. Nevertheless, it is obvious that highly characteristic recovery curves were obtained with this chemical and it showed a remarkable deviation from the reference case. For this reason, this effect should be further investigated, as this injection strategy yielded promising results (Table A.1).

Co-injection. It was shown in the reference test that the production of oil presented a linearly proportional behavior with temperature at later stages. The acceleration (or the higher slope) in the oil recovery curve can be used in the evaluation of the performance of the surfactants along with the final oil recovery.

Surfactants. By comparing the oil recoveries obtained by the sandpack experiments, it is obvious that the surfactant LTS-18 has the highest efficiency in enhancing driving forces of gravity drainage processes (Figure A.4). This surfactant was recommended for high temperature applications due to its better thermal stability compared to the other chemicals. As a result it yielded 33% more oil recovery than the reference case. The surfactant is compared to the other in the early stages very efficiently, where the production of oil resumes constant until the steam breakthrough (920 minutes).

The biodiesel achieved the second highest recovery (67%) (Table A.1). Note that biodiesel solubility in water is low and its vaporization temperature is relatively high. Therefore, one may expect an accumulation of the chemical on the top of the water phase and quick transfer of it into the system unlike other chemicals that were homogeneously dissolved in water. In the solvent (heptane) experiments, a similar reaction was observed, which is discussed in the next section. The start of the injection of the biodiesel solution caused an immediate increase in recovery. After 400 minutes a plateau was reached. After the steam breakthrough, the valve of the high temperature steam was closed because the 500ml chemical solution was not completely introduced



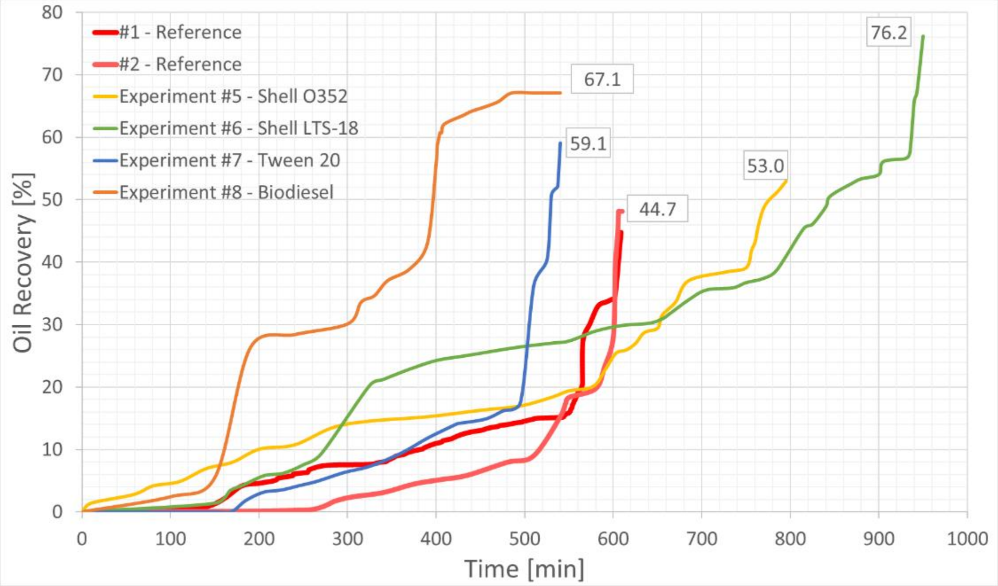


Figure A.4: Summary of the oil recoveries in the preliminary high-pressure tests using chemical additives.

into the system. During this period, temperature profiles of this experiment (Table A1) indicated that biodiesel was injected into the core at a temperature value of 120°C and no additional oil was produced. Once the steam heated the whole system, indicated by a sharp increase in the outlet temperature, oil production started rising significantly and reached its maximum. These observations indicate that biodiesel might be an effective chemical at higher temperatures (more partitioning to steam) and is introduced in the beginning part of the process. It may not be recommended for tertiary injection with wet steam (or hot-water).

Tween 20 surfactant reached the maximum capacity at high temperatures. When the whole system reached its highest temperature, Tween 20 cases generated oil recovery of 59%. The olefin

Table A.1: Overview of the core flood results oil recovery and water consumption.

Nr.	Chemical	Concentration	Oil Recovery	Water Consumption
1	Reference	-	44.7%	3200 ml
		Tertiary Injection		
2	AAS J11111 (AAS)	1 %wt.	-	-
3	AAS J11111 (AAS) + NaCl	1 %wt. + 1.5 %wt.	-	-
4	Ionic Liquid	1 %wt.	20%	500 ml
		Co-Injection		
		Surfactants		
5	O352	1 %wt.	53%	3093 ml
6	LTS-18	1 %wt.	76.2%	3538.5 ml
7	Tween 20	1 %wt.	59.1%	2791.95 ml
8	Biodiesel	1 %wt.	67%	2850 ml
		Ionic Liquid		
9	Ionic Liquid	1 %wt.	40.15%	2700 ml
		High pH Solution		
10	Sodium Metaborate ($NaBO_2$)	1.5 %wt.	45.5%	3962.64 ml
		Solvent		
11	Heptane (C_7H_{16})	1.5 %wt.	37.5%	2200 ml
		Nanoparticle		
12	Silicon Oxide (SiO_2)	1 %wt.	41.7%	1700 ml

sulfonate O352 increased the oil recovery by 8% only reaching its maximum value of 52% at the end. This indicates Tween's higher thermal stability.

High pH solution, ionic liquid, solvent, nanoparticles. As mentioned, the result of the solvent injection resembles the trend of the curve of biodiesel. A rapid oil production was observed during the injection of heptane. Note that as heptane is not soluble in water that was used to introduce it into the system to mix with steam, water and heptane "solution" was continuously stirred to prevent its accumulation at the top. Despite these efforts, however, the amount of heptane introduced is expected to be higher in the beginning due to accumulation of it at the top by gravity segregation. Production started around the same time (around 200min) like the other cases but the recovery was much faster than all others (Figure A.4). That is the period when heptane mixed with steam and helped in reducing the viscosity of oil much faster. Being identical to the biodiesel experiment, the injection was continued until the entire 500 ml solution was in the system. However, the ultimate recovery was the lowest of the all cases in Figure A.4 indicating the negative effect of solvent in the entrapment of oil as reported by Argüelles-Vivas et al. (2012). The nanoparticle silicon oxide accelerated the production much faster, which can be attributed to its positive effect on stable emulsion. Alomair et al. (2014) measured the emulsion viscosity created by the nanofluids such as silicon oxide and aluminum oxide. The additional viscosity increase of emulsions may had an impact in the acceleration of gravitational forces.

References for Chapter A

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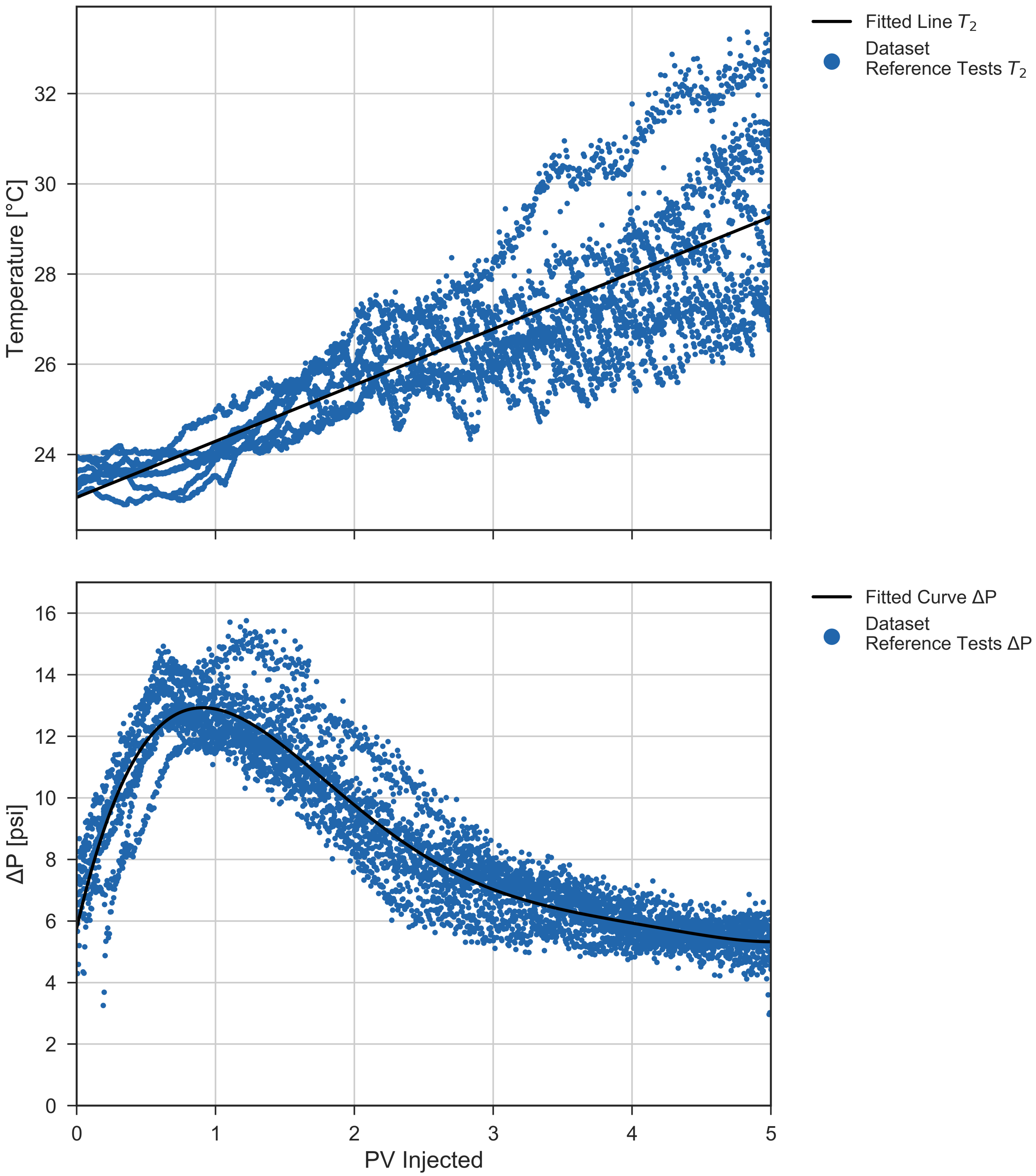


Figure A.5: Regression Analysis for the differential Pressure ΔP and Outlet Temperature T2

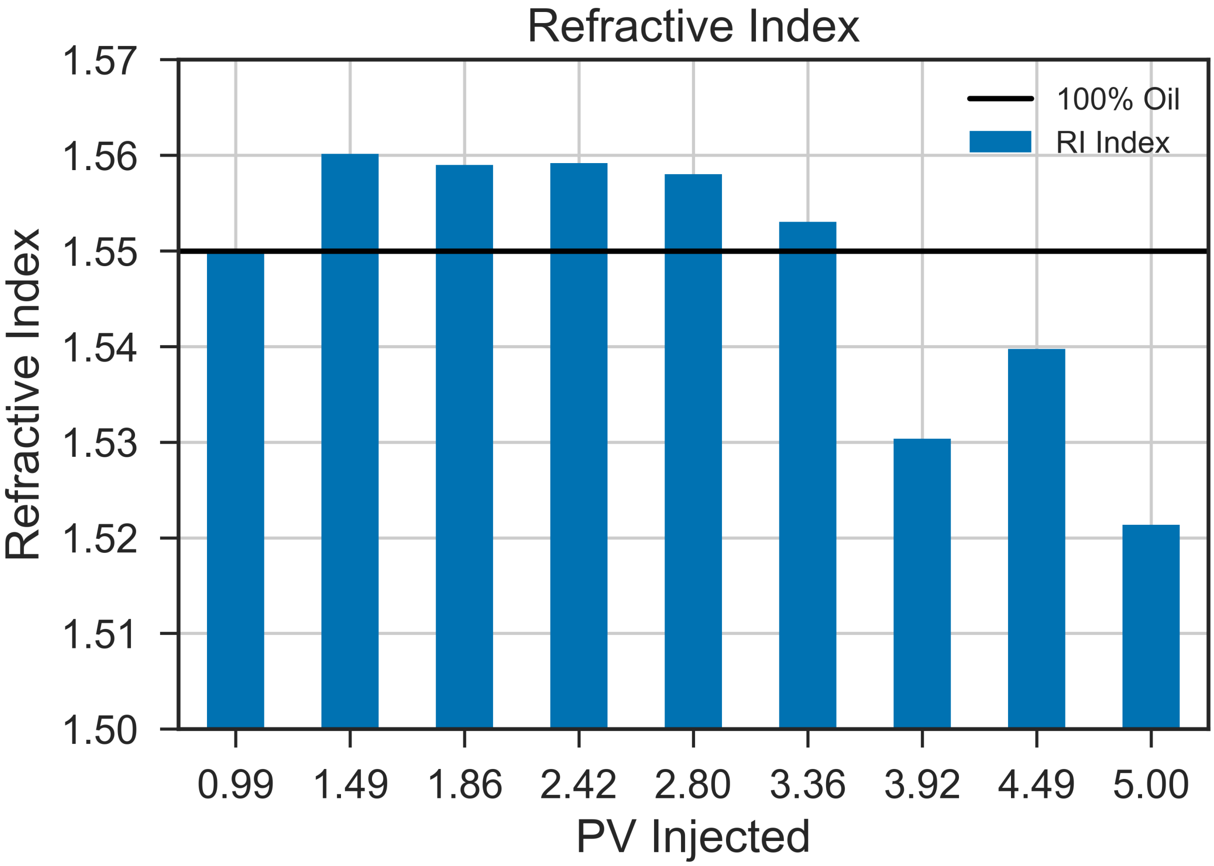


Figure A.6: Refractive Index (RI) measurements of the heptane experiment samples

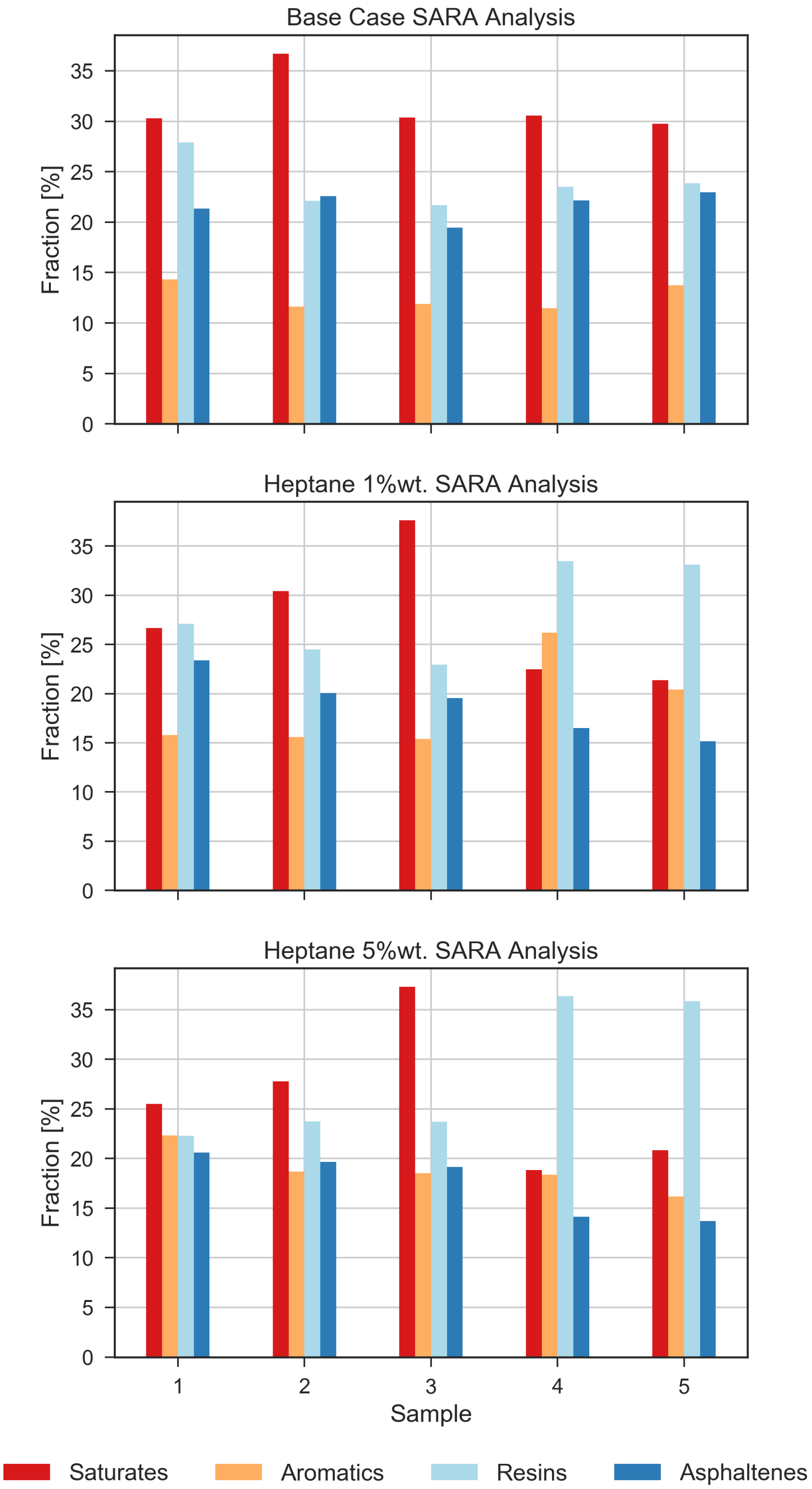


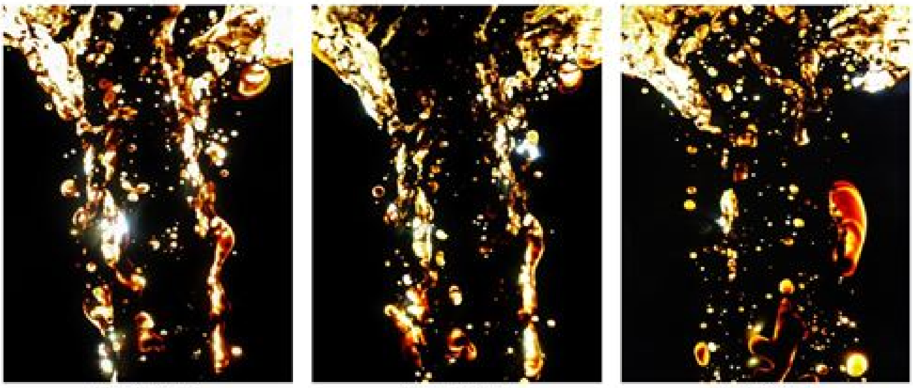
Figure A.7: SARA Analysis for samples taken from the reference test, heptane 1%wt., and heptane 5%wt. experiments

Appendix B

Chapter 3

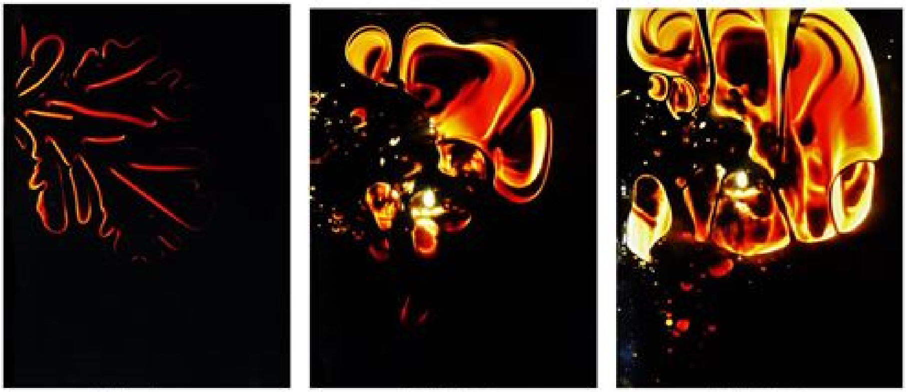
(a) T1=Start-up (b) T2=30 min (c) T3=60 min

(d) T4=90 min (e) T5=120 min (f) T6=150 min

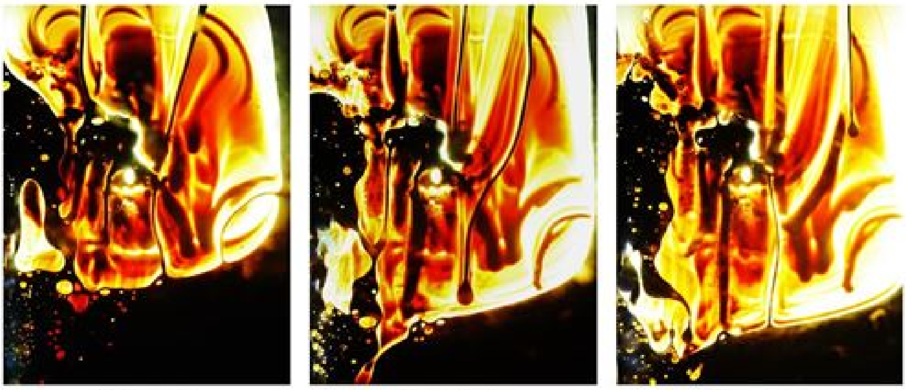


(g) T7=180 min (h) T8=210 min (i) T9=240 min

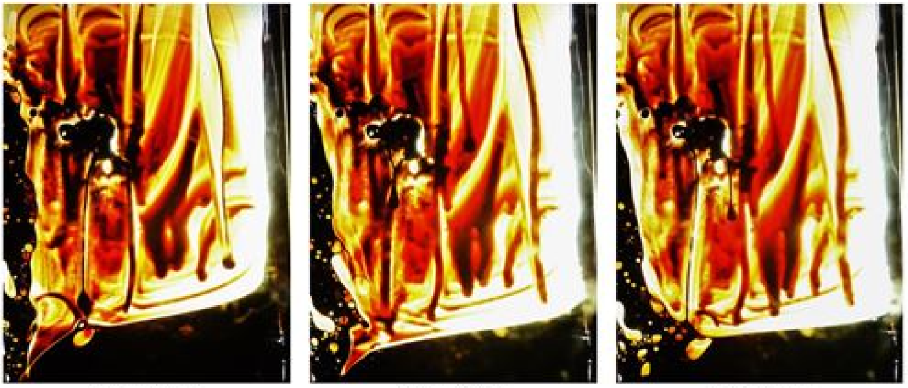
Figure B.1: Base Case experiment Set 1 at specific times.



(a) T1=Start-up (b) T2=30 min (c) T3=60 min

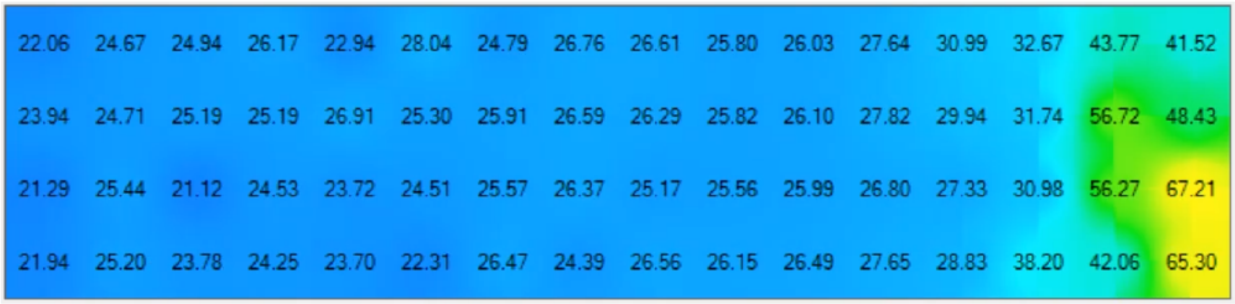


(d) T4=90 min (e) T5=120 min (f) T6=150 min



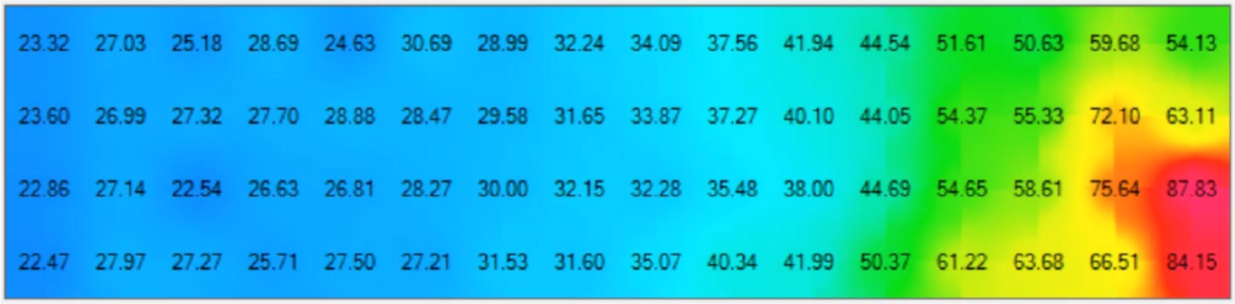
(g) T7=180 min (h) T8=210 min (i) T9=240 min

Figure B.2: Base Case experiment Set 2 at specific times.



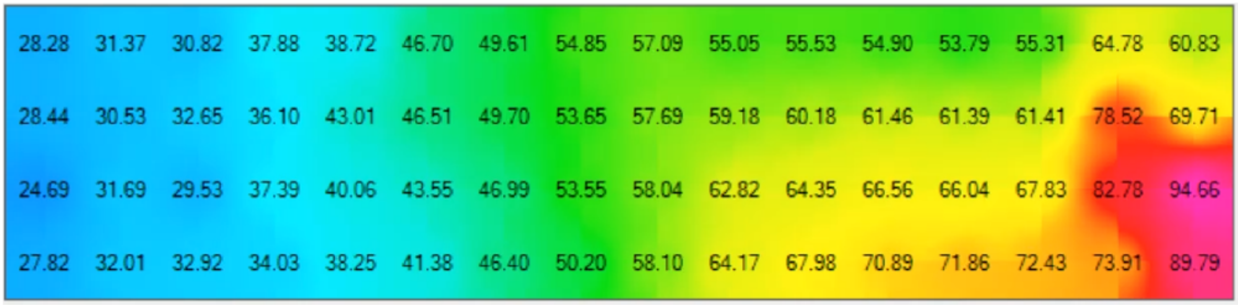
22.06	24.67	24.94	26.17	22.94	28.04	24.79	26.76	26.61	25.80	26.03	27.64	30.99	32.67	43.77	41.52
23.94	24.71	25.19	25.19	26.91	25.30	25.91	26.59	26.29	25.82	26.10	27.82	29.94	31.74	56.72	48.43
21.29	25.44	21.12	24.53	23.72	24.51	25.57	26.37	25.17	25.56	25.99	26.80	27.33	30.98	56.27	67.21
21.94	25.20	23.78	24.25	23.70	22.31	26.47	24.39	26.56	26.15	26.49	27.65	28.83	38.20	42.06	65.30

(a) T1=Start-up



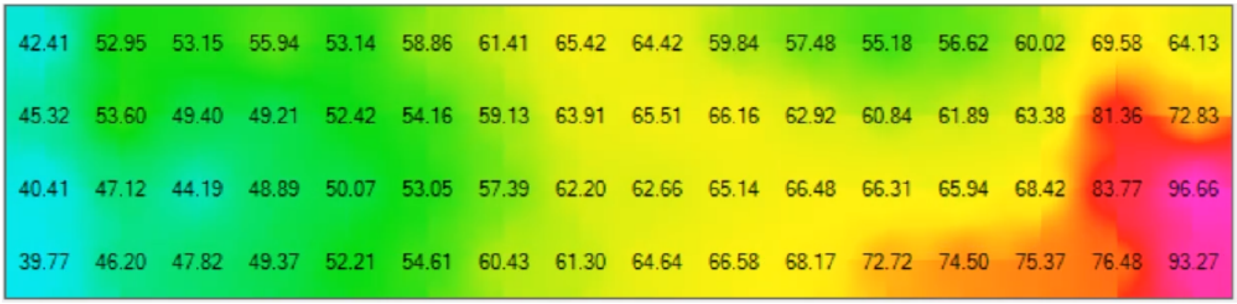
23.32	27.03	25.18	28.69	24.63	30.69	28.99	32.24	34.09	37.56	41.94	44.54	51.61	50.63	59.68	54.13
23.60	26.99	27.32	27.70	28.88	28.47	29.58	31.65	33.87	37.27	40.10	44.05	54.37	55.33	72.10	63.11
22.86	27.14	22.54	26.63	26.81	28.27	30.00	32.15	32.28	35.48	38.00	44.69	54.65	58.61	75.64	87.83
22.47	27.97	27.27	25.71	27.50	27.21	31.53	31.60	35.07	40.34	41.99	50.37	61.22	63.68	66.51	84.15

(b) T3=60 min



28.28	31.37	30.82	37.88	38.72	46.70	49.61	54.85	57.09	55.05	55.53	54.90	53.79	55.31	64.78	60.83
28.44	30.53	32.65	36.10	43.01	46.51	49.70	53.65	57.69	59.18	60.18	61.46	61.39	61.41	78.52	69.71
24.69	31.69	29.53	37.39	40.06	43.55	46.99	53.55	58.04	62.82	64.35	66.56	66.04	67.83	82.78	94.66
27.82	32.01	32.92	34.03	38.25	41.38	46.40	50.20	58.10	64.17	67.98	70.89	71.86	72.43	73.91	89.79

(c) T6=150 min



42.41	52.95	53.15	55.94	53.14	58.86	61.41	65.42	64.42	59.84	57.48	55.18	56.62	60.02	69.58	64.13
45.32	53.60	49.40	49.21	52.42	54.16	59.13	63.91	65.51	66.16	62.92	60.84	61.89	63.38	81.36	72.83
40.41	47.12	44.19	48.89	50.07	53.05	57.39	62.20	62.66	65.14	66.48	66.31	65.94	68.42	83.77	96.66
39.77	46.20	47.82	49.37	52.21	54.61	60.43	61.30	64.64	66.58	68.17	72.72	74.50	75.37	76.48	93.27

(d) T9=240 min

Figure B.3: Temperature profile of the Base Case experiment Set 1 at specific times.